THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 5 MARCH, 1937 NUMBER 3

The New Absorption System of Cyanogen Gas in the Near Ultraviolet. System I

SHO-CHOW WOO AND TA-KONG LIU
National Research Institute of Chemistry, Academia Sinica, Shanghai, China

(Received December 30, 1936)

A new system of absorption bands has been found in the region λλ3020–2400 with an absorbing path of three meters and a pressure of two atmospheres. The gross structure of the system is comparatively simple. Two main progressions of bands with frequency differences 2050 cm^{-1} and 895 cm^{-1} have been found. The bands in these progressions can be accurately represented by a general formula:

$$\nu = A + \omega_1' v_1' + x_{11}' v_1'^2 + \omega_2' v_2' + x_{22}' v_2'^2 + x_{12}' v_1' v_2'$$

with $A = 33{,}293.63$, $\omega_1' + x_1' = 895.75$, $\omega_2' = 2065.38$, $x_{22}' = -15.13$ and $x_{12}' = -8.00$. The electronic excitation is mainly at the C–N bond. The structure of the molecule in the excited state, its normal frequencies and symmetry properties are also discussed. The frequency difference 2050 cm^{-1} is considered as due to the totally symmetric longitudinal (C–N) vibration in the excited, state and a tentative assignment is suggested as follows: $\nu_1' = 895$ cm^{-1}, $\nu_2' = 2050$ cm^{-1}, $\nu_3' = 1770$ cm^{-1}, $\delta_2'(u) = 210$ cm^{-1}. Other possible assignment has also been briefly discussed.

ALTHOUGH numerous investigations of the ultraviolet absorption spectra of polyatomic molecules have been made in the past, only in a few fortunate cases have they been completely explained. The most natural attempt toward simplification is to investigate those molecules which possess a structure of high symmetry. This has actually been done in most of the successful cases. In the case of linear polyatomic molecules, great similarity of the spectra with those of diatomic molecules is to be expected. But even here, complications may come in from the increasing possibilities of excitation at different bonds, the overlapping of several electronic systems, the uncertainty concerning the structure of the molecule in the excited state, and the interaction between degenerate electronic state and deformation oscillations.

The structure of the cyanogen molecule is probably of the collinear symmetrical type. Its ultraviolet spectrum has been studied by several investigators.[1] The complexity probably lies in the overlapping of several electronic systems. With a long absorbing path, we have now found a new weak absorption system which is well separated from other electronic systems. Thus it simplifies the problem greatly. Consequently an analysis of this comparatively simple system may throw some light on the nature of excitation and the structure of the molecule in the excited state, and may facilitate the analysis of the more complicated group of bands found in the shorter wave-length region.

EXPERIMENTAL

The cyanogen gas used in the investigation was prepared in an all-glass apparatus by dropping a concentrated solution of potassium cyanide into a solution of 100 grams of copper sulphate in 200

[1] R. B. Mooney and H. G. Reid, Proc. Roy. Soc. (Edinburgh) **52**, 152 (1932); Sho-Chow Woo and Richard M. Badger, Phys. Rev. **39**, 932 (1932); T. R. Hogness and Liu-Sheng Ts'ai, J. Am. Chem. Soc. **54**, 123 (1932).

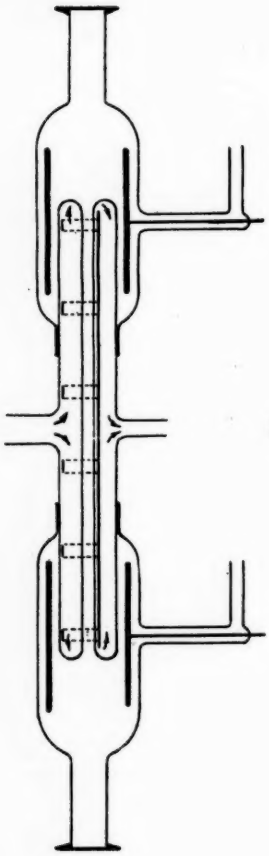


FIG. 1.

cc of water. The gas after being dried with $CaCl_2$ and P_2O_5 was collected in a trap cooled by a mixture of solid carbon dioxide and ether. The chemicals used for the preparation were of C. P. grade. Before being introduced into the absorption tube, the gas was purified by fractionation under reduced pressure. The middle portion was then collected in a liquid-air trap and subjected to thorough evacuation in order to remove any volatile impurities which might be present. The gas thus obtained could be kept for months without any sign of polymerization. Since the new bands found here began to appear only with a fairly long absorption path, the spectrum might be enormously affected by traces of impurities which might be present in the sample. In order to insure the purity of the cyanogen gas and to verify the real absorber of these bands, preparations from different sources were considered necessary, especially when one notices the fact that potassium cyanide, even of the highest C. P. grade, does not have a purity higher than 98 percent. Two samples were thus prepared, one by heating C. P. mercuric cyanide and the other by the process described above, using in place of potassium cyanide, a mixture of aqueous potassium hydroxide and hydrogen cyanide which was freshly prepared and purified before use. The samples prepared by these different methods did not show any difference in the spectrum. This may be considered a strong evidence for the purity of the gas. In order to avoid any complication coming in due to the presence of mercury vapor, plates were also taken without using a Hg manometer.

The experimental arrangement was as usual. The hydrogen discharge tube used as the continuous light source had the construction shown in Fig. 1. The whole apparatus was made of Pyrex glass and consisted of two parts, the inner discharge tube and the electrode compartments, joined together with cement which had been proved to have no effect on the purity of the spectrum. The inner tube which had an internal diameter of 5 mm, was silvered and provided with a cooling device. The special advantage of this type of tube lies in its simplicity of construction. Broken parts could be replaced and assembled within one or two hours and moreover it possesses the merit of high intensity which characterizes the types suggested by Bay and Steiner and by Kistiakowsky. The provision of two end windows is recommended for facilitating the line-up with the optical axis of the spectrograph. In the present experiment, the tube was excited with a 1 kva transformer at 3000 v in the secondary.

The spectrum was taken with a Bausch and Lomb large Littrow type spectrograph which has a dispersion of 4.2A/mm at 3000A and 1.2A/mm at 2040A. We are quite satisfied with the instrument except that when it was set for the region λλ2400–2000, the optical system was in such a position that the light of longer wave-lengths dispersed from the system fell upon the wall of the instrument and was reflected directly on to the central portion of the photographic plate. Thus the spectrum was considerably affected by this stray light in a one-hour exposure. This defect was effectively removed by inserting in the instrument a diaphragm which cut off com-

pletely the reflected beam without any effect on the incident light.

Glass tubes of 50 cm and 150 cm long, fitted with quartz windows, and connections to traps, manometer and vacuum pump, were used as absorption cells. For pressures greater than one atmosphere, a 3 m copper tube provided with screwed-on windows was employed. The pressure of the absorbing gas varied from 0.5 mm to about one atmosphere in the case of the shorter tubes, and from one to two atmospheres in the case of the longer tube. It was found that the nature of part of the bands varied greatly with the amount of the absorbing gas. Plates were taken at adjusted pressure intervals in order to develop the systems as completely as possible. Ilford Empress and Eastman 33 and 40 plates were used. Iron arc and copper spark lines were used as comparison spectra.

Measurement of the bands was made with an S.I.P. comparator. The error of measurement for bands above λ2100 was less than ± 1 cm^{-1} while for those below λ2100 it might be somewhat greater. Microphotometer tracings were also made with a Kipp and Zonen instrument.

Results and Discussion

With the above described experimental conditions, there were obtained in the region λλ3020–2030 more than 900 bands including those in the region λλ2300–2030 reported by previous authors. However, since we used higher dispersion and finer adjustment of the pressure, the number of bands in the latter region increased considerably and many of them were much better resolved. The bands on the red side of λ2300 began to appear and extended already to λ3020 when the pressure was one atmosphere with an absorption path of 150 cm. On doubling both the pressure and absorption path, little further extension was observed except the appearance of additional weaker bands in this region.

The possibility of ascribing these high pressure bands to molecules other than cyanogen, present as impurities, appears to be excluded by the careful purification of the sample and also by the fact that the different samples prepared by quite different methods gave the same spectrum. Furthermore they cannot very well be due to the CN molecule which might have been formed by photochemical dissociation for two reasons. First of all, if any CN molecules were formed in a concentration sufficiently high to give these bands, it would certainly be high enough to show the CN red and violet systems, which were certainly absent in our present case. In the second place it is impossible for any diatomic molecule to give

Table I. *The cyanogen bands in the region λλ3020–2480, system I.*

λ(A) (in Air)	ν(cm^{-1}) (in Vacuum)	I	Designation	λ(A) (in Air)	ν(cm^{-1}) (in Vacuum)	I	Designation
3024.6	33053	0		2618.4	38180	0	
3006.9	33247	1		2617.0	38200	1	
3004.7	33272	2		2616.0	38215	0	
3002.7	33294	3	a_0	2614.0	38244	4	b_2
2925.5	34172	0		2555.6	39118	2	
2924.1	34189	1	b_0	2544.4	39290	0	
2853.7	35031	0		2543.9	39299	0	
2852.6	35045	0		2540.3	39354	5	a_3
2851.0	35065	2		(2520.1)	(39669)	1	
2849.1	35088	1		(2519.6)	(39677)	1	
2834.0	35276	2		(2518.7)	(39691)	1	
2831.1	35312	3		(*R*2510.0)	(39829)		
2828.6	35343	5	a_1	(*V*2509.2)	(39841)	1	
2780.3	35957	0		(*R*2509.0)	(39844)		
2764.3	36165	0		(2508.6)	(39851)	7	
2763.8	36172	0		(*V*2508.5)	(39853)		
2762.4	36190	0		(*R*2508.4)	(39854)		
2762.0	36195	0		(*V*2507.5)	(39868)	7	
2761.3	36205	2		(2507.1)	(39874)	5	
2760.0	36221	00	b_1	2505.4	39902	0	
2759.2	36232	3		2491.2	40129	0	
2698.5	37047	1		2490.8	40136	0	
2695.6	37087	0		2490.4	40142	0	
2693.4	37116	0		2489.4	40158	0	
2684.2	37244	0		2488.6	40171	0	
2680.8	37291	1		2487.9	40182	0	
2678.5	37323	4		2485.3	40225	2	b_3
2675.6	37364	6	a_2				

Table II. *Main progressions in C_2N_2, system I.*

ν(cm^{-1})	Δν		ν(cm^{-1})	Δν		
a_0 33722 } 22			b_0 34172 } 17			
33294 }			34189 }			$b_0-a_0=895$
35312 } 31	2049		36205 } 27	2043		
a_1 35343 }		28	b_1 36232 }		31	$b_1-a_1=889$
37323 } 41	2021		....?	2012		
a_2 37364 }		31	b_2 38244		31	$b_2-a_2=880$
39299? } 55	1990		....?	1891		
a_3 39354 }			b_3 40225			$b_3-a_3=871$

Table III.

n_1'	n_2'	ν (obs.)	ν (calc.)
0	0	33294	33293.6
	1	34189	34189.5
1	0	35343	35343.9
	1	36232	36231.6
2	0	37364	37363.9
	1	38244	38243.6
3	0	39354	39353.6
	1	40225	40225.4

rise to bands forming regular progressions with two normal frequencies (see below).

In Table I are given only the wave-lengths and wave numbers of those bands in the region λλ3020–2480 where most of them constitute a well defined system (which will be designated as C_2N_2 system I) with very little overlapping. They are considered to belong to a separate electronic system for the following reasons. Firstly, they form regular progressions with reasonable intensity distribution and converging intervals, which cannot be extended to bands on the shorter wave-length side. Secondly, the frequency separations between bands in the progressions are definitely smaller than the corresponding ones of the other systems. Only the bands of system I will be discussed here while those in parentheses are of another electronic system and will be reported together with the low pressure bands which are still under investigation.

Most of the bands in system I are rather sharp and narrow. They degrade very slightly toward the red, showing a very slight increase of moment of inertia by the excitation. Some of them, e.g., a_0, a_1, a_2, $a_3(?)$, b_0 and b_1 appear to be doublets with separations increasing toward the high frequency side. Two main progressions of regular intensity distribution are given in Table II. These bands can be fitted into a general formula:

$$\nu = A + \omega_1' v_1' + x_{11}' v_1'^2 + \omega_2' v_2' + x_{22}' v_2'^2 + x_{12}' v_1' v_2' \quad (1)$$

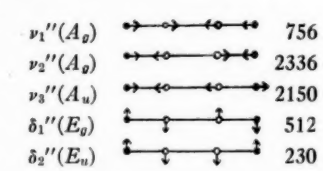
with $A = 33{,}293.63$

$$\omega_1' + x_{11}' = 895.75, \quad x_{12}' = -8.00$$
$$\omega_2' = 2065.38, \quad x_{22}' = -15.13.$$

The calculated and observed wave numbers are given in Table III.

Before any meaning can be ascribed to the frequency differences 2049 cm^{-1} and 895 cm^{-1}, a discussion of the structure of the molecule, the normal frequencies in the ground state and the symmetry properties is necessary. The zero electric moment of the molecule points to a symmetrical structure. From the result of electron diffraction, Wierl[2] suggested for the structure of the molecule in the ground state a model with the two CN radicals bent in a transposition. The result can, however, be more plausibly explained by a symmetrical collinear model as shown by Brockway.[3] This latter model is also supported by the results of infrared and Raman spectra. Thus the molecule in the ground state should have a symmetry, $D_{\infty h}$. There are two vibrations having the symmetry A_g, and three others having respectively the symmetry A_u, E_g and E_u. Only the two A_g vibrations are totally symmetrical and nondegenerate with respect to all the symmetry elements. If the molecule in the excited state has the same symmetry as that in the normal state, it will be seen that only these two totally symmetrical vibrations can undergo any change of quantum number during the electronic transition, although the unsymmetrical, nondegenerate and the degenerate vibrations may change their quantum numbers with certain restrictions which depend upon the nature of the electronic states taking part in the transition.[4] This means that from the symmetry considerations alone, only the frequencies of these totally symmetrical vibrations will appear strongly in the spectrum.

We have previously had occasion to discuss the normal frequencies of the cyanogen molecule in the ground state and have assigned the following values:[5]



From what has been said above, it will be seen that the frequency difference 2049 cm^{-1} found in our main progression must be the frequency ν_2' of the totally symmetrical vibration in the excited state and hence the electronic excitation must have taken place mainly at the C–N bond.

Difficulties have been experienced in assigning the frequency difference 895 cm^{-1}. The most natural assignment is $\nu_1' = 895$ cm^{-1}. If this is the case, the electronic excitation must have affected both the C–N and C–C bonds with a

[2] R. Wierl, Ann. d. Physik **13**, 453 (1932).

[3] L. O. Brockway, Proc. Nat. Acad. **19**, 868 (1933).

[4] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

[5] Sho-Chow Woo, Ta-Kong Liu and T. C. Chu, J. Chinese Chem. Soc. **3**, 301 (1935).

TABLE IV. *Bands with 1770 cm^{-1} and 1980 cm^{-1} separations.*

35045 / 33272 — 1773	35031 / 33053 — 1978	38180 / 36195 — 1985
35065 / 33294 — 1771	35276 / 33294 — 1982	38200 / 36221 — 1979
35957 / 34189 — 1768	36172 / 34189 — 1983	38215 / 36232 — 1983
37047 / 35276 — 1771	37047 / 35065 — 1982	40158 / 38180 — 1978
37087 / 35312 — 1775	37291 / 35312 — 1979	40182 / 38200 — 1982
37116 / 35343 — 1773	37323 / 35343 — 1980	

result of weakening the former and strengthening the latter simultaneously. A detailed calculation on the variation of ν_2/ν_1 with $\gamma=k_2/k_1$ and $\delta=k_3/k_1$ (where k_1 and k_2 are, respectively, the force constants of the C−C and C−N bonds while k_3 denotes the force constant accounting for their mutual interaction, the interaction between the two C−N bonds being neglected) shows that in order to have $\nu_2'/\nu_2'=2049/895 \doteq 2.3$, the interaction between the C−C and C−N bonds must have also been increased to a considerable degree.

A physical interpretation of the above results may be found on the basis of Pauling's theory of resonance. This has been done by Brockway[3] in interpreting his electron diffraction results, where the molecule of cyanogen in the ground state is regarded as having a structure formed mainly by the resonance of the following two structures with I predominant.

$$:\!N\vdots\!\vdots\!C:C\vdots\!\vdots\!N:\qquad\qquad :\dot{N}::C::C::\dot{N}:$$
$$\text{I.}\qquad\qquad\qquad\text{II.}$$

Now if the electronic excitation is such that the molecule in the excited state is brought to a structure with II predominant, our results—the weakening of the C−N bond and the strengthening of the C−C and of the interaction between C−C and C−N can be satisfactorily explained.

Since the electronic excitation has affected the C−N bond, the frequencies ν_3' and $\delta_2'(u)$ (or strictly $2\nu_3'$, $2\delta_2'(u)$ and $\nu_3'+\delta_2'(u)$) may have the possibility of appearing in the spectrum. As a matter of fact, we have found weaker bands with frequency differences 1770 cm^{-1} and 1980 cm^{-1} (Table IV). The former may be considered as ν_3' and the latter as the sum of ν_3' and $\delta_2'(u)$, although the selection rules of Herzberg and Teller[4] are not strictly followed here. The decrease of ν_3 from 2150 cm^{-1} to 1770 cm^{-1} by the electronic excitation is just what should be expected from the above interpretation.

TABLE V. *Force constants of the cyanogen molecule.*

STATE	k_1 (C−C)	k_2 (C−N)	k_3
Ground state	5.13×10^5	17.48×10^5	0.099×10^5 dyne/cm
Excited state	8.3×10^5	11.8×10^5	0.87×10^5 dyne/cm

It may be of interest to see how the force constants of the different bonds have been changed by the electronic excitation. Calculation has thus been carried out for both of the normal as well as the excited states. The results are given in Table V.[6]

It will be seen that the above interpretation explains satisfactorily nearly all the experimental results. However, it still leaves some of the weak bands on the red side of the main bands untreated. An alternative interpretation has thus been tried by regarding 895 cm^{-1} as $2\delta_1'(g)$ and setting the selection rule $\Delta v_{\delta_1}'=$odd, which may be true for a forbidden transition. The bands a_0 and b_0 are considered as due to transitions from the vibrationless level in the ground state to levels in the excited state with v_{δ_1}' excited by 1 and 3. A combination of this assumption with $\nu_2'=2049$, $\nu_3'=1770$, $\delta_2'(u)=210$ and $\delta_2''(u)=230$ may reproduce all of the bands to within 10 cm^{-1}. However, from the selection rule and intensity considerations, this is quite improbable.

In conclusion the authors want to express their sincere thanks to Professor Richard M. Badger for his kindness in reading the manuscript before publication and to Dr. Ny Tsi-Zé and Mr. S. C. Tsien for the preparation of the microphotometer curves. Our thanks are also due to Mr. T. C. Puan for his assistance in making the preliminary experiments with the Hilger E1 of the Physics Institute.

[6] It may be admitted that the neglect of the interaction between the two C−N bonds may introduce appreciable error for the case of the excited state. However, not all of the four constants can be evaluated directly from the three frequencies. The calculation may be accurate enough for our present purpose where only the approximate values of the K's are needed.

The Raman Spectra of Water, Aqueous Solutions and Ice

JAMES H. HIBBEN
Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.
(Received November 9, 1936)

The Raman spectra of water at different temperatures, of aqueous solutions and of ice have been discussed in detail. Several low frequency shifts such as $\Delta\tilde{\nu}$ 150, 445 and the shift at 2170 are easily discernible if ultraviolet excitation is used. The first two of these vary markedly in intensity with temperature changes and are affected by some solutes. All three are present in ice at slightly displaced frequencies. At least some of these frequencies may be ascribed to the intermolecular influences. Whatever may be the mechanism of polymerization or association these results indicate that effectively such a state exists and is a function of environmental conditions.

INTRODUCTION

THE most consistently divergent results in any Raman spectra studies have been those obtained from the investigation of water. This is primarily attributable to the unique broadness of the bands observed. Theoretically water vapor has three fundamental frequencies, namely, $\Delta\tilde{\nu}$ 1595 (δ_π) for the transverse oscillation or the bending motion of the hydrogen atoms, $\Delta\tilde{\nu}$ 3600 (ν_π) for their symmetrical oscillation in a linear direction along the line of the valence bonds and $\Delta\tilde{\nu}$ 3757 (ν_σ) for the asymmetrical oscillation of the atoms in the molecules. Part of the difficulty has been that not all of these are active either in infrared absorption spectra or in Raman spectra. Furthermore, from the latter point of view there appear possibly three bands in the $\Delta\tilde{\nu}$ 3400–3600 region for the liquid. This is not observable in the infrared absorption as the dipole moment change is small. On the other hand, $\Delta\tilde{\nu}$ 3756 is not observed at this frequency in the Raman spectra for either the liquid or vapor but appears as $\Delta\tilde{\nu}$ 3630 in the liquid and 3654 in the vapor. The conclusion possibly has been reached that the multiplicity of bands observed in liquid water owe their origin to the existence of several molecular species, the interaction giving rise to a perturbation of the normal frequency shifts. Whether or not they are physically distinct species or are the result of hindered rotation or translation is still unsettled. The effect, however, in either case is that the interaction between adjacent water molecules is far from negligible and there is a pronounced effect upon the Raman spectra obtainable. This is supported in no small degree by the existence of other Raman shifts in the frequency range between $\Delta\tilde{\nu}$ 60 and 1600 which cannot be accounted for by the vibrations of a classical oscillator of the type XY_2.

HIGH FREQUENCY SHIFTS FOR THE WATER BANDS

The results obtained up to 1934 have been summarized in detail by the writer.[1] The earlier work, principally by I. R. Rao, indicated three Raman frequencies in the region of $\Delta\tilde{\nu}$ 3220, 3420 and 3630 corresponding to the symmetrical vibrations of the hydrogen atoms. The exact maxima estimated by visual inspection by different observers varied over a range of 50 or more wave numbers. The advent of more accurate determinations through microphotometric means has materially reduced the discrepancies.

Unfortunately from the point of view of simplicity of interpretation neither the intensity nor the maxima of the bands $\Delta\tilde{\nu}$ 3220–3630 remain constant. They are influenced both by dissolved electrolytes and temperature. Rao,[2] Meyer[3] and Ganesan and Venkateswaran[4] early observed that an increase in temperature caused a diminution in the intensity of $\Delta\tilde{\nu}$ 3220 frequency and an increase for $\Delta\tilde{\nu}$ 3630. The opposite effect has been observed in going from water to ice. The effect of solutes is generally somewhat similar to that of a temperature increase.[5–7] The evidence for the

[1] Hibben, Chem. Rev. **13**, 345 (1933).
[2] Rao, Indian J. Phys. **3**, 123 (1928).
[3] Meyer, Physik. Zeits. **31**, 510 (1930).
[4] Ganesan and Venkateswaran, Indian J. Phys. **4**, 195 (1930).
[5] Hibben, Proc. Nat. Acad. Sci. **18**, 532 (1932).
[6] Brunetti and Ollano, Atti accad. Lincei **12**, 522 (1930).
[7] Ollano, Zeits. f. Physik **77**, 818 (1932).

existence of a band at $\Delta\tilde{\nu}$ 3630 is dependent mainly upon a very small break in the curves concomitant with a marked shift in the position of the central band. It is difficult, therefore, to decide whether this is indicative of a change in the position of the maxima of the band or an augmentation in the intensity of the highest frequency. Early observers and more recently Magat[8] failed to observe any band at $\Delta\tilde{\nu}$ 3630. On the other hand, Carelli and Cennamo[9] consider the principal water band made up of three components $\Delta\tilde{\nu}$ 3110, 3400 and 3590. The extensive work of I. R. and C. S. Rao[10–13] also indicates three bands.

Low Frequency Shifts for the Water Bands

Segrè,[14] Bolla,[15] Magat[16a, b] have indicated frequencies less than $\Delta\tilde{\nu}$ 1600. These are $\Delta\tilde{\nu}$ 60, 140–172, 510–780. From the published microphotometric curves the frequencies of $\Delta\tilde{\nu}$ 60 and 780 are very doubtful, as will be seen later. Nevertheless it is of considerable importance to confirm the existence of these and other frequencies mentioned and this has been one of the purposes of this investigation. There is no doubt that low frequency oscillations do exist at $\Delta\tilde{\nu}$ 150 and 445.* This is likewise true of $\Delta\tilde{\nu}$ 2170, the last frequency having been noted before only by Bolla.[17] Owing to their extreme weakness none of the frequencies below $\Delta\tilde{\nu}$ 3220 was observed with accuracy until the advent of ultraviolet excitation, although it was postulated[6] that a frequency at $\Delta\tilde{\nu}$ 1600 should exist, and indeed it was early observed by Kimura and Uchida[18] and by da Silveira.[19] The $\Delta\tilde{\nu}$ 500–700 bond is claimed by Magat[20] to show an anomalous disappearance at 37°C. This is disputed by Bolla.[21]

Other shifts supposedly observed, namely, $\Delta\tilde{\nu}$ 3990,[17] 984,[22] 2355,[4] 4023 and 5100[8] and a group observed by Hulubei[23] extending from $\Delta\tilde{\nu}$ 6747 to 10944 have been postulated but are doubtful.

At least one low frequency shift occurs in liquid D_2O, namely, $\Delta\tilde{\nu}$ 178 in water.[24–26] This is not appreciably displaced from its position. On the contrary the high frequencies in the $\Delta\tilde{\nu}$ 3400–3600 group are shifted very much lower in D_2O. Depolarization measurements on water and deuterium oxide by Ananthakrishnan[24] indicate

[8] Magat, J. de phys. et rad. **5**, 347 (1934).
[9] Carelli and Cennamo, Nuovo cimento **10**, 329 (1933).
[10] I. R. Rao, Phil. Mag. **17**, 1113 (1934).
[11] I. R. Rao, Proc. Roy. Soc. (London) **A145**, 489 (1934).
[12] C. S. Rao, Proc. Roy. Soc. (London) **A151**, 167 (1935).
[13] C. S. Rao, Phil. Mag. **20**, 310 (1935).
[14] Segrè, Atti accad. Lincei **13**, 929 (1932).
[15] Bolla, Nuovo cimento **9**, 290 (1932).
[16a] Magat, Comptes rendus **196**, 1981 (1933).
[16b] Magat, Ann. d. Physik **6**, 108 (1936).

* The determination of the absolute maximum of a band located on the downward slope of a larger band is subject to considerable error. The maxima as given here differ slightly from those estimated by others. This is without great significance.

[17] Bolla, Nuovo cimento **10**, 101 (1933).
[18] Kimura and Uchida, Japan J. Phys. **5**, 97 (1928).
[19] da Silveira, Comptes rendus **195**, 652 (1932).
[20] Magat, J. de phys. et rad. **6**, 179 (1935).
[21] Bolla, Nuovo cimento **12**, 243 (1935).
[22] Johnston and Walker, Phys. Rev. **39**, 535 (1932).
[23] Hulubei, Comptes rendus **194**, 1474 (1932).
[24] Ananthakrishnan, Proc. Indian Acad. Sci. **3A**, 201 (1936).
[25] Ananthakrishnan, Proc. Indian Acad. Sci. **2A**, 201 (1935).
[26] Magat, Comptes rendus **201**, 667 (1935).

TABLE I. *Raman spectra of water, ice, solutions and hydrates.*

Water 28°		Water 88°		Ice		NaOH 1 molal		NaOH 1.4 molal		$Ba(OH_2)$ 0.175 molal		LiCl 7.1 molal		KBr 2.8 molal		$MgCl_2$ 1.7 molal		$MgCl_2 \cdot 6H_2O$		$CdSO_4 \cdot 8/3H_2O$†	
$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i	$\Delta\tilde{\nu}$	i
144	(1)	149	(00)			145	(00)			160	(0)	150	(2)	128	(2)	130	(2)				
				205	(4)																
440	(4)	450	(2)			450	(1)	450	(0)	450	(2)	450	(2)	465	(4)	474	(4)				
				601	(3)																
1627	(3)	1629	(3)	—		1629	(2)	1629	(0)	1629	(2)	1629	(2)	1630	(5)	1625	(4)				
2170	(2)	2118	(3)			2140	(1)	2140	(0)	2135	(1)	—		2157	(3)	2165	(3)				
				2225	(2)																
				3136	(10)																
3219	(8)	3222	(5)			3220	(7)	3216	(5)	3215	(9)	3236	(5)	3206	(7)	3202	(7)				
				3330	(8)													3372	(8)	3346	(5)
3445	(10)	3460	(10)			3450	(10)	3460	(10)	3450	(10)	3450	(10)	3471	(10)	3450	(10)			3424	(8)
																		3514	(8)		

† The shifts for cadmium sulfate proper are not included in this table. There is no evidence for any un-ionized magnesium chloride.

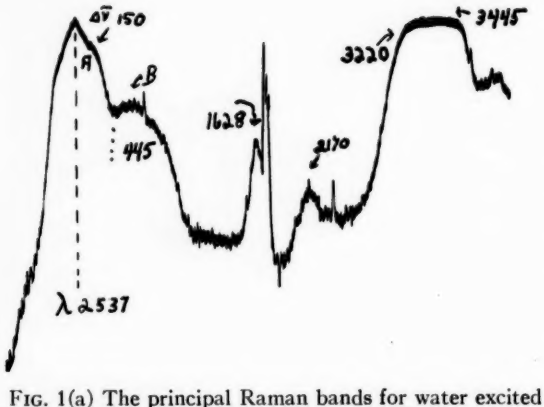


FIG. 1(a) The principal Raman bands for water excited by the 2537A mercury line, namely, $\Delta\tilde{\nu}$ 150, 445, 1628, 2170, 3220, 3445, which are, from left to right, indicated by arrows.

Fig. 1 (a) shows four different water bands in addition to the $\Delta\tilde{\nu}$ 3220–3630 shifts. These are: $\Delta\tilde{\nu}$ 150, 445, 1628, 2170. That $\Delta\tilde{\nu}$ 150 is genuine is indicated in 1 (b) which shows an expanded tracing of this portion of the band. Fig. 2 shows the effect of temperature on the lower frequency bands. Fig. 3 shows the remarkable effect of adding small quantities of alkali. Fig. 4 indicates the effect in 2.8 molal solution of KBr, 1.7 molal $MgCl_2$, and 7.1 molal LiCl, respectively, and Fig. 5 shows the water bands in $MgCl_2 \cdot 6H_2O$ and $CdSO_4 \cdot 8/3\ H_2O$ crystals whose shifts are, respectively, $\Delta\tilde{\nu}$ 3387 and 3507, 3348 and 3426. In the last illustration are shown the results of experiments with ice, including the shifts at $\Delta\tilde{\nu}$ 205, 601 and 2225 (Fig. 6).

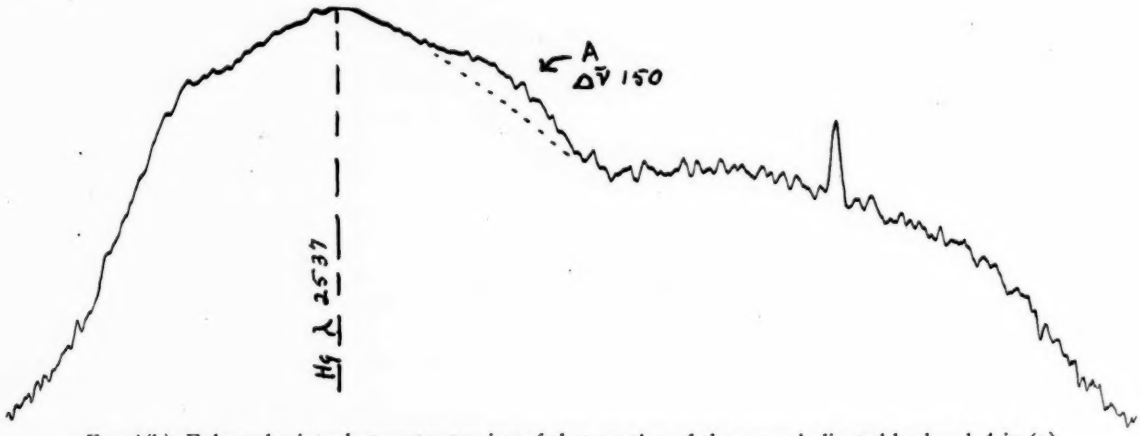


FIG. 1(b). Enlarged microphotometer tracing of that portion of the curve indicated by band *A* in (a).

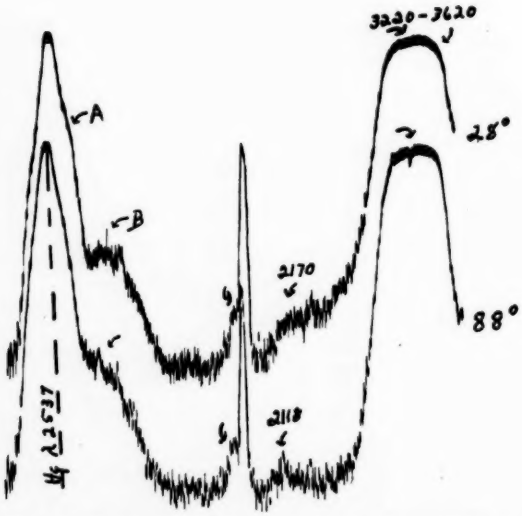


FIG. 2. The decrease in intensity of the water bands $\Delta\tilde{\nu}$ 150 and 445 as a function of increased temperature is indicated.

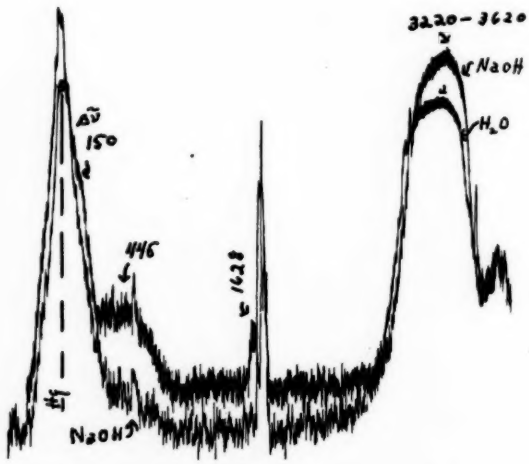


FIG. 3. A comparison between the Raman spectrum of pure water and a 5 percent solution of NaOH.

an increase in the value of ρ with an increase in the frequencies of the Raman shifts in this region. Consequently $\Delta\tilde{\nu}$ 3630 should correspond to the ν_a—the asymmetrical type of vibration. The $\Delta\tilde{\nu}$ 178 (150) also has a maximum depolarization.

Structure of Water

The modification of the Raman frequencies with varying temperatures and solutes has been the subject of investigation by I. R. Rao,[10] C. S. Rao,[12] Segrè,[14] Hatley and Callihan,[27] Specchia[28] and others. In general the observations have been confined to the $\Delta\tilde{\nu}$ 3200–3600 band. The explanation of the modifications in this band is largely based on a change of the number of water polymers, i.e., such as H_2O, $(H_2O)_2$ and $(H_2O)_3$, the normal unpolymerized water giving rise to the high frequency shift $\Delta\tilde{\nu}$ 3630 (cf. $\Delta\tilde{\nu}$ 3654 for water vapor). Bernal and Fowler[29] have proposed a quasicrystalline arrangement for water having respectively a tridymite, quartz and close-packed ideal structure as a function of increasing temperatures. The difference between these con-

[27] Hatley and Callihan, Phys. Rev. **138**, 909 (1931).
[28] Specchia, Nuovo cimento **7**, 388 (1930).
[29] Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).

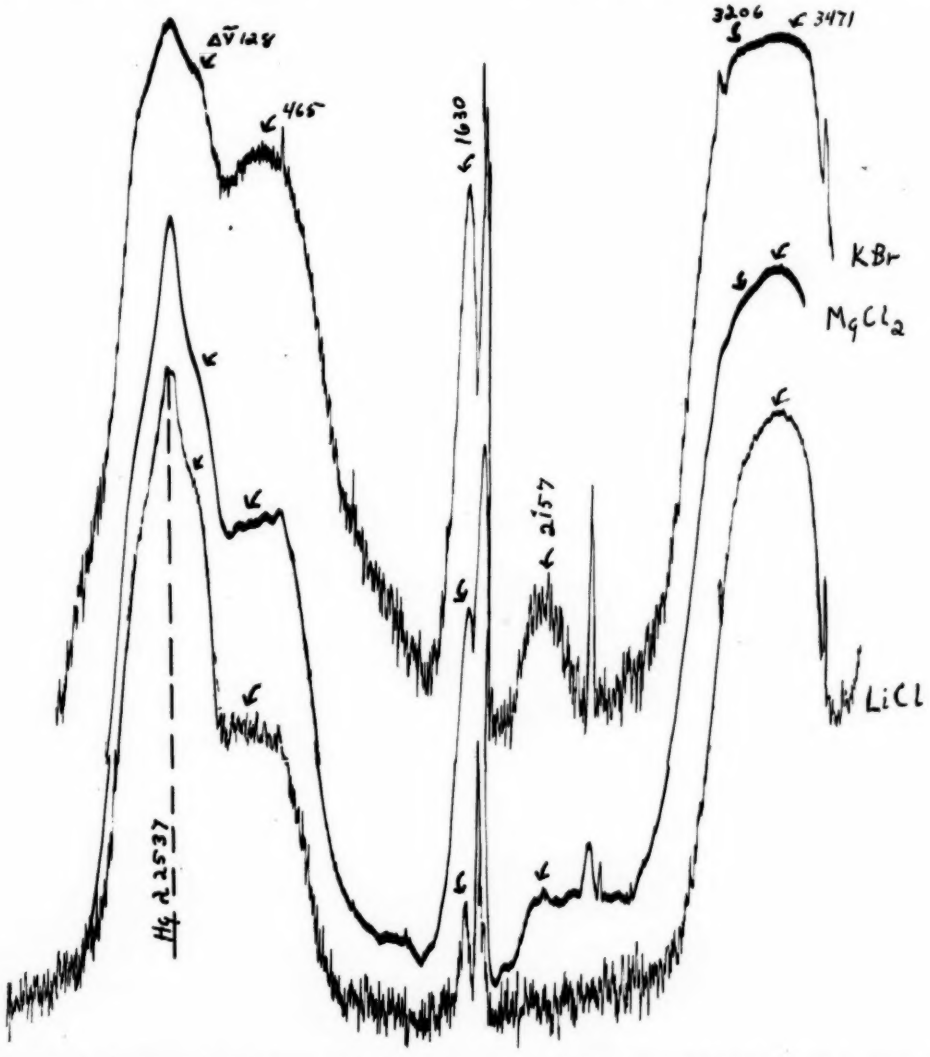


Fig. 4. A comparison between solutions of 2.8 molal KBr, 1.7 molal $MgCl_2$, and 7.1 molal LiCl. There is no marked difference between these curves and that for pure water taken under the same conditions.

cepts is more illusory than real. The essential fact is that in either case there will be a profound influence on the Raman spectra as the changes in the constitution of the water take place.

Experimental Results

The object of the experimental work to be described was first, to clarify some of the discrepancies in the reported Raman frequencies and, second, to investigate the "association" of water with particular emphasis on those lines which should be most sensitive to intermolecular perturbation—the low frequency shifts. The studies have been carried out on water at different temperatures, on crystal hydrates, solutions and ice.

It should be pointed out that the experimental procedure employed is of paramount importance. Microphotometric curves alone are without great significance. In these experiments it has been attempted to reproduce the conditions of illumination so that the same number of quanta strike the same number of water molecules under comparable conditions. On each plate developed a reference standard of the water spectrum was also made. The maximum and minimum excursions of the galvanometer while tracing the plates were adjusted so as to give the same displacement. Without such precautions it is easily possible to confuse the experimental results and subsequent interpretations.

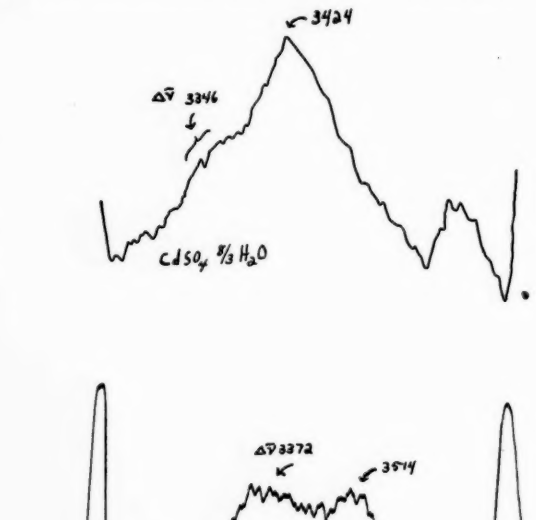


Fig. 5. Water of crystallization in $MgCl_2 \cdot 6H_2O$ and $CdSO_4 \cdot 8/3\ H_2O$ yields two lines each corresponding to the O↔H oscillation, but differing markedly both in the magnitude of the displacement and the relative intensities.

For those substances, such as acetic acid, and solutions of lithium chloride, which showed some absorption in the ultraviolet, it is necessary to take this absorption into account. These results are *not* indicative of small changes in scatterings. It is only when the modifications have reached a degree considerably beyond the experimental error that they have been held to be significant.

The results are indicated graphically in the accompanying figures, and tabularly in Table I.

Discussion

It is to be noted that the shifts at $\Delta\tilde{\nu}$ 150 and 445 in water decrease in intensity with an increased temperature and O↔H shifts are at least two in number, $\Delta\tilde{\nu}$ 3220 and 3445. The maximum of the last band shifts to a higher frequency with an increase in temperature and the intensity of the $\Delta\tilde{\nu}$ 3220 simultaneously diminishes. It is not possible from these or other curves obtained in the course of this investigation to say with certainty that $\Delta\tilde{\nu}$ 3630 is present.

The addition of any NaOH and $Ba(OH)_2$ markedly diminishes the intensity of the low frequency shifts whose very existence can be solely attributed to intermolecular interaction.

Apparently, therefore, the function of the hydroxyl ion is to decrease polymerization rather than to increase hydration. The low frequency bands are nearly completely eliminated with a 1.4 molal solution of sodium hydroxide and are markedly diminished with a 1.0 molal solution. A 0.175 molal solution of barium hydroxide also diminishes the intensity of these bands, but in a lesser degree. It is evident that one hydroxyl ion is capable of depolarizing a large number of water molecules. This seems to be at variance with the hypothesis of Bernal and Fowler,[29] who indicate that an OH ion should give greater coherence to the water structure.

The effect of salts containing both large and small anions and cations on the water is not marked. The frequency shifts $\Delta\tilde{\nu}$ 150 and 445

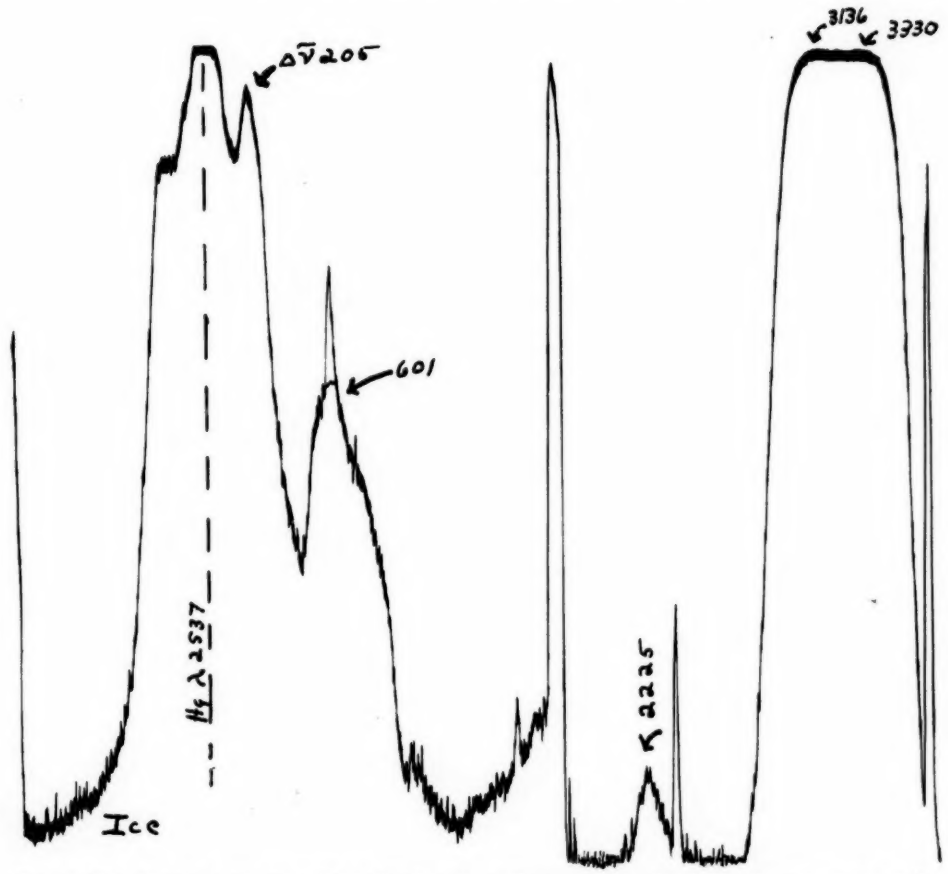


FIG. 6. The Raman spectrum of ice showing the enhancement in intensity of some of the shifts as a result of intermolecular interaction.

persist in solutions of magnesium chloride, lithium chloride and potassium bromide. The accuracy of intercomparing these curves is not sufficiently great to warrant a definite statement of the relative effects of these compounds. As compared with the alkali hydroxides, however, the difference is very marked.

Any expected effect as to the lowering of the structural temperature of the solution by ions of small radii, as postulated by Bernal and Fowler, is not realized. The persistence of the frequencies whose origin is attributed to intermolecular effects in these solutions does not point to any pronounced dissociation of the structural complex with large ions or any pronounced increase in regularity of arrangement with small ions.

The band occurring at $\Delta\tilde{\nu}$ 2118 may be a result of the combination between $\Delta\tilde{\nu}$ 445 and the fundamental at $\Delta\tilde{\nu}$ 1629. It is also interesting to note that this frequency is nearly equal to the difference between the fundamental at $\Delta\tilde{\nu}$ 3756 active in the infrared and inactive in Raman spectra and a combination of two $\Delta\tilde{\nu}$ 1650 frequencies ($\nu_a - 2\delta_\pi$).

Further evidence for the assignment of the low frequency vibrations (hindered translation and rotation) to intermolecular complexes is obtained from the spectrum of ice which is known to be polymerized. In addition to the frequencies noted by others there appear $\Delta\tilde{\nu}$ 205, 601, 2225. The first two of these are obviously slightly shifted frequencies occurring in water and appear with great strength, the first frequency showing an anti-Stokes line.

The spectra obtained from water of hydration do not have maxima identical with those of liquid water and the maxima alter from crystal to crystal. For the hexahydrate of magnesium chloride there appear two maxima, $\Delta\tilde{\nu}$ 3372 and 3514 of nearly equal intensity. For cadmium sulfate

8/3 hydrate the maxima are, respectively, $\Delta\tilde{\nu}$ 3346 and 3424 with a great disparity in intensities of the two shifts. The influence of the configuration of the crystals is evidently reflected in a change in force constant between the hydrogen and oxygen atoms.

The accuracy of determining the maxima of the extremely broad O↔H oscillations does not permit too much weight to be placed on reasonable variations in the magnitude of these shifts. This may be said also of the lowest frequencies. In the case of ice, however, there is a genuine displacement of the maxima, and the change in the magnitude of $\Delta\tilde{\nu}$ 2170 between hot and cold water is likewise real.

Summary

The Raman shifts obtained from water, ice and some solutions have been investigated particularly from the point of view of the low frequency oscillations. These could not be present in the spectrum of a simple unhindered triatomic molecule and their existence is explicable only as a result of intermolecular interaction regardless of the precise mechanism of such interaction. The greatly enhanced intensities of these lines in ice as compared with water furnish reasonably conclusive evidence that the assignment of these frequencies to intermolecular coupling is proper. Moreover their alteration in intensity in the liquid phase with temperature variations is consistent with the concept of structural changes in the liquid as a function of temperature. In solution, however, the results are not in entire agreement with the lowering of the structural temperature of the solutions by ions of small radii or with an equivalent elevation in temperature by ions of large radii. New frequencies are reported for ice and the existence of a shift at $\Delta\tilde{\nu}$ 2170 for water has been found to be genuine. Other low frequencies noted by a few observers have been confirmed.

MARCH, 1937 JOURNAL OF CHEMICAL PHYSICS VOLUME 5

Infrared Absorption Spectra of Four Grignard Solutions*

William Byrle Plum
Southwestern College, Winfield, Kansas

(Received May 18, 1936)

Absorption spectra are reported for twelve liquids: four typical Grignard solutions, and eight related substances, for the range 1.0 to 13 μ. Absorption frequencies at 784, 910, 4250 and possibly 1950 cm.$^{-1}$ appear to be associated with compounds which contain magnesium. Possible origins of these frequencies are discussed.

Introduction

THE infrared absorption spectra of twelve compounds, including four typical Grignard solutions, are reported in this paper, for the range from 1 μ to 13 μ. The primary purpose of the work was to determine the wave-lengths at which selective absorption occurs, in several Grignard compounds. This work is part of a broad study of a number of the physical properties of such compounds, which has been carried on under the leadership of Professor R. T. Dufford; it is hoped that eventually it may prove to be possible to correlate these properties with the very interesting photovoltaic effects which have been shown[1] to exist in solutions of Grignard compounds.

Grignard compounds are prepared in anhydrous ethyl ether solution, by the action of magnesium metal on various organic halides.

Table I.

Region	Wave-lengths	Cell Thickness	Slit Width
1.	1.0– 1.9 μ	1.00 cm	0.025 cm
2.	1.9– 4.5 μ	0.032 cm	0.030 cm
3.	4.5– 9.0 μ	0.026 cm	0.035 cm
4.	9.0–13.0 μ	0.016 cm	0.065 cm

* Abstracted from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Missouri.

While some of these compounds can be crystallized out, into crystals containing ether of crystallization, most of the work done on them is done with ether solutions. In any case, they are so readily attacked by oxygen and by water that they must be carefully shielded from contact with the atmosphere; this condition multiplies the difficulties of studying them. It is true that absorption spectra of vapors may be more instructive, generally; but in the case of compounds such as these, which are not known to exist in the vapor state, it seems necessary to be satisfied with spectra obtained from their solutions. The photovoltaic properties mentioned above are, of course, also properties of the solutions.

Experimental

A Wadsworth type of prism-mirror spectrometer, equipped with a 60° rocksalt prism, was used. The instrument was designed by Professor Dufford, and was built by Mr. Gus Tornsjo, instrument maker at the University of Missouri. A great advantage of such an instrument is that, since all the focusing is done by mirrors, the spectrometer can be adjusted by means of visible light, such as the green mercury line; it will then be in adjustment for all wave-lengths.

A street lamp with a linear tungsten filament was used as a source of light for the region 1.0 to 4 μ. For longer wave-lengths, which would be cut off by glass, a Nernst glow lamp was used. The sensitive element of the outfit was a vacuum linear thermopile built by Dr. W. W. Coblentz, of the National Bureau of Standards. A Leeds and Northrup type HS galvanometer was used with this thermopile. The galvanometer deflections, and also the prism settings, were read by lamp and scale. A calibration table similar to that made by Cross[2] was made and used. The calibration was checked frequently.

After preliminary trials, it was found desirable to take the readings for each spectrum in four parts, each of which required about four hours of observing time for completion. Numerous check runs were made, every spectrum being observed at least twice. Actually, several spectra would be studied in a given range before going on to the next, to avoid frequent resetting of slits, etc. The wave-lengths covered in each part, together with the slit widths and cell thicknesses used, are given in Table I.

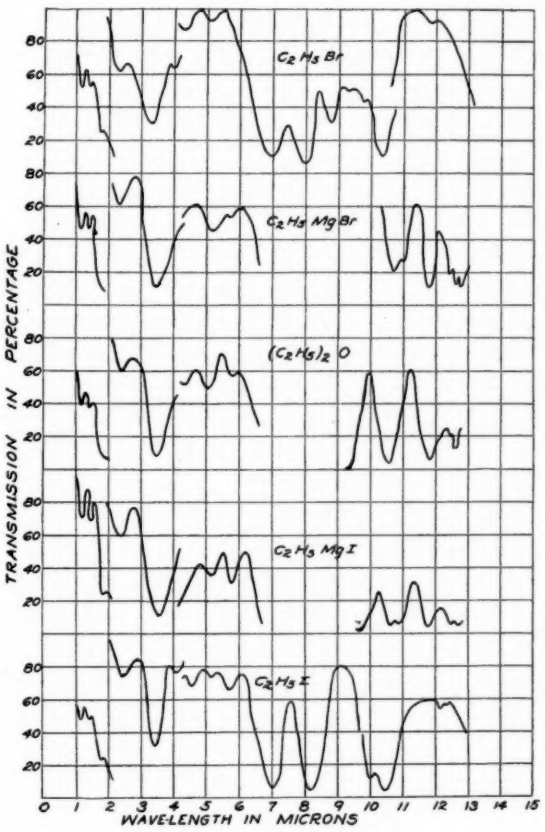


Fig. 1.

The increased slit widths which were made necessary at longer wave-lengths by the decreasing energy of the source in this part of the spectrum, are about balanced by the increased dispersion; so that the slit widths used correspond approximately to a range of from 0.001 to 0.003 μ. The rear slit was set at approximately the same width as the entrance slit. The thinner cells had rocksalt windows separated by wire spacers; it would be very difficult to work with much thinner layers of liquid. In taking readings, the energy transmitted was compared with that transmitted by a similar dummy cell, so that any possible absorption by the windows would be eliminated. With an empty dummy cell, this method introduces a slight error due to the fact that the reflection losses in each cell are not quite equal. This error varies continuously with the wave-length; and a slight further error might enter on

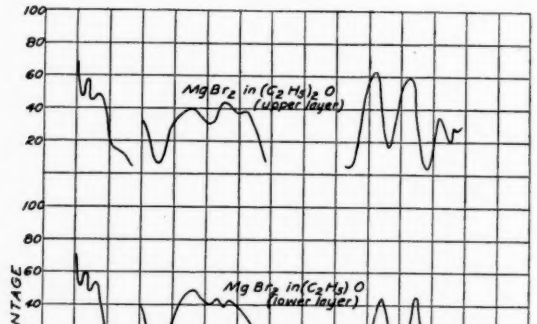


FIG. 2.

account of the fact that the light passing through the cells was not quite parallel. Hence extinction coefficients computed from these data might be in error by two or three percent. Since the amount of time needed to determine these corrections accurately for all wave-lengths for each compound would be prohibitive, and since they are not necessary for the purpose of locating wave-lengths of selective absorption, these small corrections were neglected. Curves were plotted showing the percentage transmission of the cell as compared with the dummy cell, and the intensity of the absorption bands was then expressed qualitatively on a scale of 0 (barely perceptible) to 3 (very intense).

RESULTS

In the following paragraphs, the results for individual compounds are given first; then the results for the Grignard compounds are discussed collectively.

Ethyl ether, $(C_2H_5)_2O$

Results for this substance are stated first, since it is the solvent for all the Grignard solutions Absorption bands were found with the points of most intense absorption at the following wave numbers; the relative intensities are given in parentheses: 8680 (1), 7190 (1), 5850 (0), 4330 (2), 2896 (3), 2255 (0), 1978 (1), 1720 (1), 1032 (3), 843 (3), 802 (1), 796 (2). The four highest frequencies are pretty certainly combination or overtone bands. The intense band centered at 2896 cm^{-1} is known[19] to be a fundamental associated with the C−H linkage. The absorption here is so intense that the ether is practically opaque; even with a cell of only 0.016 cm thickness, and with wide slits, no transmission above 10 percent was obtained in the region from 6.8 to 9.5 μ. While the necessity for leaving this gap in the spectra of ether and the ether solutions is regretted, the lack is less serious than at first appears; for it is known from the Raman effect[19] that the frequencies which characterize ether in this region are at 2980, 2930, and 2870 cm^{-1}, and there is small reason to expect anything else in this region except possibly unimportant combination bands. The identification of the remaining bands is not essential for present purposes.

Ethyl bromide, C_2H_5Br

This substance might be present in ethyl magnesium bromide solution as an impurity, if the reaction which formed the Grignard compound did not go to completion. It is therefore necessary to have its spectrum for comparison. Absorption bands were found at the following wave numbers: 8880 (1), 7300 (1), 5840 (0), 4410 (1), 2910 (3), 2520 (1), 2300 (1), 1980 (0), 1920 (0), 1740 (0), 1430 (3), 1257 (3), 1123 (2), 1065 (1), 1018 (0), 967 (3), 844 (1). Cross and Daniels[4] have reported an additional band at 1385 cm^{-1}, which was not observed in the present work.

While this compound contained no ether, the similarity of its spectrum to that of ether is striking, the same frequencies frequently occurring in both spectra. This is just what should be expected; for the hydrocarbon part of both molecules is the same. The differences between the spectra should be due to the substitution of the C−Br bond for the C−O bonds of the ether.

Similar remarks apply in the case of the following compounds also.

Ethyl iodide, C_2H_5I

This substance might be present in ethyl magnesium iodide solution as an impurity, if the reaction which formed the Grignard compound did not go to completion. It is therefore desirable to have its spectrum for comparison. Absorption bands were found at 8850 (1), 7140 (1), 5720 (0), 4205 (2), 2940 (3), 2430 (1), 2196 (1), 1960 (1), 1727 (2), 1428 (3), 1211 (3), 1010 (1), 961 (3), 855 (0), 840 (0), 825 (1), and 806 (0). An additional band at 1380 cm^{-1}, reported by Cross and Daniels,[4] was not observed in this work. This spectrum is strikingly like that of ether and that of ethyl bromide, for the reasons suggested in the preceding paragraph.

Ethyl magnesium bromide, C_2H_5MgBr, in ether solution

This is one of the typical Grignard solutions studied. Structurally, the compound differs from ethyl bromide, discussed above, by the insertion of the magnesium atom between the bromine atom and the ethyl radical. This solution, like all the other Grignard solutions discussed, had a concentration of approximately one mole per liter. Absorption bands were found as follows: 8550 (1), 7030 (1), 4250 (2), 2870 (3), 1990 (0), 1955 (2), 1740 (1), 1665 (0), 932 (3), 908 (3), 843 (3), 802 (1), 796 (2), and 784 (2). Of course, this spectrum shows the frequencies of the solvent ether; but many of these should be equally characteristic of the Grignard compound also, as they were of the other compounds discussed above. It is of course impossible to state to what extent any of these is to be attributed to the Grignard compound. However, the bands at 784, 908, 4250, and possibly 1955, did not appear in any of the preceding spectra, and hence appear to belong definitely to the Grignard compound, and to be there because of the introduction of the magnesium atom into the molecule. They will be discussed later on, in connection with the results from the other Grignard compounds.

Ethyl magnesium iodide, C_2H_5MgI, in ether solution

This is another typical Grignard solution, differing from the last only in that it contains iodine instead of bromine. Absorption bands were found at 8550 (1), 6890 (1), 5410 (0), 4255 (2), 2870 (3), 1970 (1), 1715 (2), 1033 (3), 938 (3), 914 (3), 844 (3), 798 (0), and 783 (1). As with the preceding compound, many of the frequencies that are certainly due in part to the solvent ether are probably also partly due to the Grignard compound too. But, just as in the preceding case, there are frequencies at 783, 914, 4255, and possibly 1970, which appear to belong to the Grignard compound, and not to any of the related compounds previously discussed. The band at 1950 cm^{-1} is close to a weak ether band, so that its exact location and identification are somewhat uncertain.

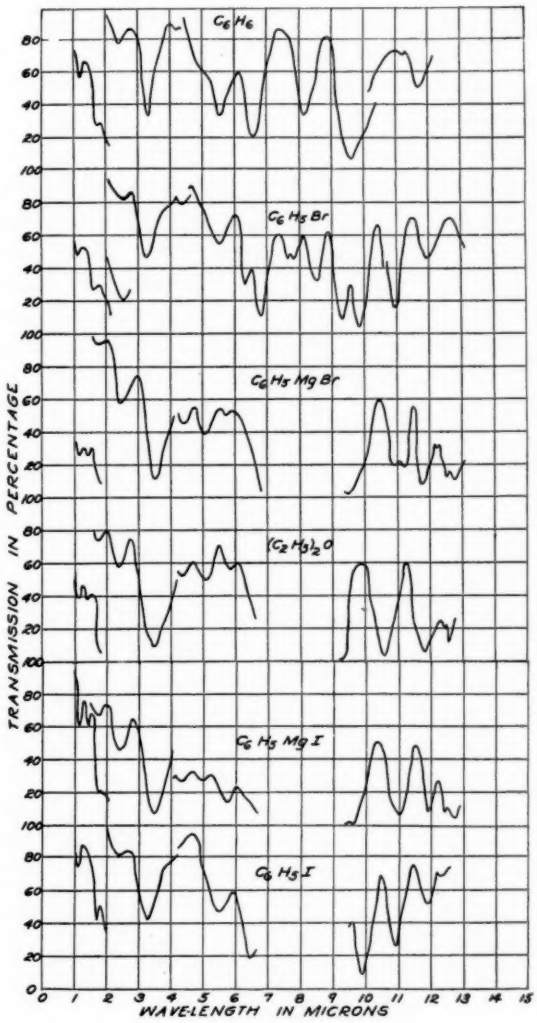


FIG. 3.

Magnesium bromide, in ether solution; $MgBr_2 \cdot 2(C_2H_5)_2O$

This substance is a possible impurity in certain of the Grignard solutions, as the result of possible side reactions. For the present work, it was prepared by the action of magnesium on "ethylene bromide" (dibromoethane), in ether solution. The solution separates into two layers, the upper layer being clear and colorless, the lower dark brown and nearly opaque. The lower layer contains about twenty times as high a concentration of $MgBr_2$ as the upper; the $MgBr_2$ crystallizes easily from the lower layer, forming transparent colorless crystals which contain ether of crystallization. Both the crystals and the solution react vigorously with water, which apparently replaces the ether associated with the $MgBr_2$ molecules. For the lower layer, bands were found at 8620 (1), 7040 (1), 2900 (3), 1930 (2), 1790 (1), 1027 (3), 907 (3), 840 (2), 793 (2), and 778 (1). All of these are ether bands except those at 778 and 907 cm^{-1}, which are the same as the lowest frequencies that appeared to belong to the Grignard compounds discussed above. These will be discussed further later on. The results from the upper layer are the same, except that the non-ether bands are weaker.

Iodine, in ether solution

This is another possible impurity in certain Grignard solutions. While the iodine solutions are somewhat more opaque in the infrared than pure ether, they do not show any new bands; no bands were found that did not clearly belong to the solvent ether. Coblentz[6] has shown that bromine solutions behave similarly. Hence it seems permissible to conclude that neither of these substances, if present, would give rise to any bands which could mistakenly be attributed to the Grignard compounds, in the region studied here.

Benzene, C_6H_6

The results on this compound are not new; they are quoted partly because of the interest in comparing benzene itself with the derivatives discussed below, and partly because they will enable the reader to judge as to the accuracy of the present work by comparing these results with those of other observers. The absorption bands found were at 9050 (1), 5780 (0), 4130 (1), 3030 (3), 2410 (0), 1802 (2), 1500 (3), 1233 (3), 1042 (3), 897 (1), 857 (2), 806 (1) cm^{-1}. It is interesting to point out how, when the symmetry of the benzene molecule is destroyed by substituting a halogen for one of the hydrogen atoms, certain bands which are single in benzene become double in the spectra of the derivatives. Thus, the 1042, 1233, and 1500 cm^{-1} bands of benzene are replaced by doublets in the two following derivatives.

Bromobenzene, C_6H_5Br

This compound might be present as an impurity in certain Grignard solutions if the reac-

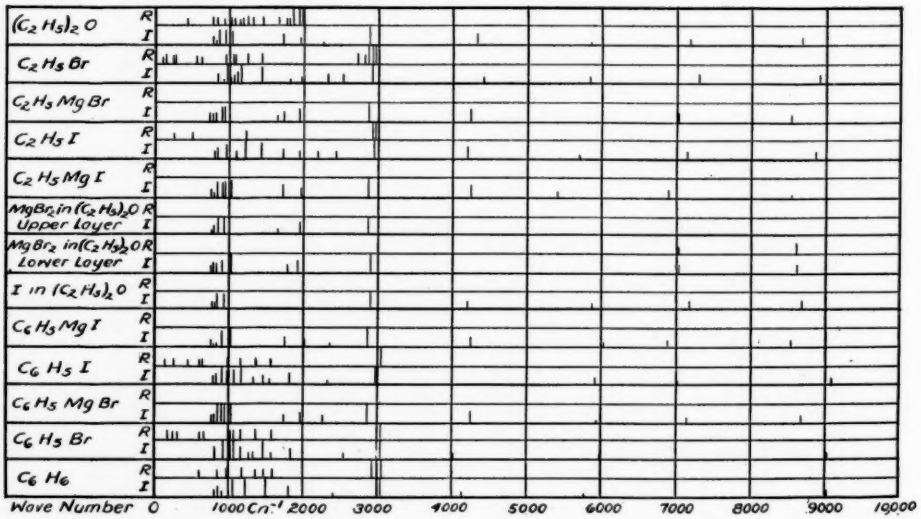

(C2 H5)2 O
C2 H5 Br
C2 H5 Mg Br
C2 H5 I
C2 H5 Mg I
MgBr2 in (C2 H5)2 O Upper Layer
MgBr2 in (C2 H5)2 O Lower Layer
I in (C2 H5)2 O
C6 H5 Mg I
C6 H5 I
C6 H5 Mg Br
C6 H5 Br
C6 H6
R
I
Wave Number 0 1000 Cm-1 2000 3000 4000 5000 6000 7000 8000 9000 10,000

FIG. 4.

tion failed to go to completion. Its spectrum is therefore given for comparison. Its absorption bands were found at 9020 (1), 5980 (0), 4000 (1), 3060 (3), 2545 (1), 1833 (1), 1577 (1), 1473 (3), 1315 (1), 1280 (1), 1170 (2), 1075 (3), 1015 (3), 914 (3), 837 (2), and 793 (0). In this compound, the 1042 cm^{-1} band of benzene is replaced by bands at 1015 and 1075; the 1233 band by bands at 1170 and 1280; and the 1500 band by bands at 1473 and 1577 cm^{-1}.

Iodobenzene, C_6H_5I

Since this compound is one that might be present as an impurity in certain Grignard solutions, its spectrum is given for comparison. Absorption bands were found at 9090 (1), 7030 (0), 5920 (1), 4000 (1), 2990 (3), 2330 (0), 1823 (2), 1563 (1), 1470 (2), 1340 (1), 1265 (0), 1177 (2), 1069 (3), 1010 (3), 913 (3), 837 (2), 789 (1). In this compound, the 1042 cm^{-1} band of benzene is replaced by bands at 1010 and 1069; the 1233 band by bands at 1177 and 1265; and the 1500 band by bands at 1470 and 1563 cm^{-1}, just as was found in bromobenzene above. While some of these bands are fairly intense, no one of them was found in the spectra of the corresponding Grignard solutions; hence it seems possible to conclude that the Grignard solutions were not badly contaminated by unreacted bromobenzene or iodobenzene, respectively.

Phenyl magnesium bromide, C_6H_5MgBr, in ether solution

This is one of the typical aromatic Grignard solutions studied. Absorption bands were found at 8680 (1), 7140 (1), 5950 (0), 4255 (2), 2870 (3), 2270 (1), 1980 (2), 1740 (1), 1040 (3), 913 (3), 890 (3), 843 (3), 820 (0), 798 (1), 784 (1). Most of these bands coincide with bands due to the solvent ether or with bands due to the parent bromobenzene (which could not have been present in large quantity); but probably most of these bands are just as characteristic of the Grignard compound as of the other compounds, on account of the similarity of structure. There are three bands, at 784, 913 and 4255 cm^{-1}, which do not appear in the spectra of the related compounds, and which therefore appear to belong to the Grignard compound. They agree with the bands found in the spectra of the aliphatic Grignard compounds already discussed.

Phenyl magnesium iodide, C_6H_5MgI, in ether solution

This is another typical aromatic Grignard compound in solution. Absorption bands were found at 8550 (1), 6890 (1), 6020 (0), 4250 (2), 2870 (3), 2360 (0), 2020 (1), 1765 (2), 1032 (3), 907 (3), 841 (2), 798 (0), and 784 (1). As in the preceding compound, there are bands at 784, 907, and 4250 cm^{-1} which appear to belong to the Grignard compound.

In order to make possible a further check on the results presented in this article, curves showing the experimental results on the aliphatic Grignard compounds and their related substances are included in Fig. 1; Fig. 2 are the curves for the substances magnesium bromide and iodine that are related to both groups of Grignard compounds. Fig. 3 shows the curves for the aromatic Grignard compounds and their related substances. Fig. 4 shows how the observed infrared frequencies compare with those found by various workers for the same substances, in the Raman effect. The check is close for the aliphatic compounds, but less so for the aromatic compounds.

To summarize the results for the Grignard compounds: it is probable that the group of frequencies that persist through ether, ethyl bromide, etc., or through benzene, bromobenzene, etc., being associated with the hydrocarbon part of the molecules, are equally characteristic of the Grignard compounds also; but the present method of attack does not lend itself readily to proof of this. Outside of these, there remain the bands at approximately 784, 910, 4250, and possibly 1955 cm^{-1} to be explained One suggestion is that they are ether bands which have been shifted because of the material in solution. If so, the unmodified ether bands appear along with them. The 4250 band appeared in all the spectra of Grignard solutions, and nowhere else. It is no doubt a combination band of some sort, but further statements appear unjustified at present. The 1955 band, which is also no doubt some kind of combination band, is more doubtful; it appeared only in the spectra of the aliphatic Grignard solutions, and it may possibly be an ether band. The bands at 784 and 910 require further attention. In addition to the possibility pointed out above, there are at least two other explana-

tions which seem not to be ruled out by the present evidence. It may be pointed out that they are not associated with the C—Mg linkage, since they appear in the spectra of the $MgBr_2$ solutions. They might be associated with motion along the Mg—Br linkage (according to the view of Dadieu and Kohlrausch[19]), since this linkage exists in all the compounds which gave these bands. Against this explanation are the arguments that the frequencies are higher than would be expected from such motion, unless these are overtone or combination bands, and that the frequencies are so nearly alike in bromine and iodine-bearing compounds. There is some evidence for this explanation, however, from the Raman effect in similar compounds.[3] Another possible hypothesis is that they are associated with the etheration structure which chemists believe is common to all the compounds studied which gave these bands. On this view, the correct formulas for the compounds would be $C_2H_5MgBr \cdot 2(C_2H_5)_2O$, $C_2H_5MgI \cdot 2(C_2H_5)_2O$, $C_6H_5MgBr \cdot 2(C_2H_5)_2O$, etc. Again the frequencies seem higher than would be expected from such a structure. Until the spectra can be explored further into the infrared, so that possible lower frequencies can be investigated, it seems best to leave open the question as to the origin of these bands.

The author wishes to acknowledge the assistance received from the members of the department of physics of the University of Missouri where this work was done, and to make special acknowledgment of the help and guidance received throughout the work from Professor R. T. Dufford, who suggested the problem and directed the work.

Bibliography

1. R. T. Dufford, J. Phys. Chem. **34**, 1544 (1930); **35**, 988 (1031); **37**, 709 (1933).
2. P. C. Cross, Rev. Sci. Inst. **4**, 197 (1933).
3. C. E. Cleeton and R. T. Dufford, Phys. Rev. **37**, 362 (1931).
4. P. C. Cross and F. Daniels, J. Chem. Phys. **1**, 48 (1933).
5. E. B. Wilson, Phys. Rev. **45**, 706 (1934).
6. W. W. Coblentz, *Investigations of Infrared Spectra* (1905), p. 61.
7. R. Bowling Barnes, Phys. Rev. **35**, 1524 (1936); **36**, 296 (1936).
8. R. B. Barnes, W. S. Benedict and C. M. Lewis, Phys. Rev. **47**, 129 (1935).
9. J. F. Daugherty, Phys. Rev. **34**, 1540 (1929).
10. R. Deslandres, Compt. rendus **192**, 120, 521 (1931).
11. J. W. Ellis, Phys. Rev. **22**, 200 (1923).
12. A. Kratzer, Zeits. f. Physik **3**, 289 (1920).
13. P. Lambert and J. Lecomte, Ann. de physique **18**, 329 (1932); Compt. rendus **192**, 96 (1932).
14. C. E. Leberknight, Phys. Rev. **43**, 967 (1933).
15. R. E. Robertson and J. J. Fox, Proc. Roy. Soc. **A120**, 128, 149 (1928).
16. S. Silverman, Phys. Rev. **34**, 1549 (1929).
17. A. L. Ruark and H. C. Urey, *Atoms, Molecules, and Quanta* (McGraw-Hill Co., Inc., New York, 1930).
18. C. E. Cleeton, Thesis, University of Missouri (1930).
19. A. Dadieu and K. W. F. Kohlrausch, J. Opt. Soc. Am. **21**, 286 (1931).
20. R. T. Dufford, Phys. Rev. **47**, 199A (1935).
21. H. A. Kramers and W. Heisenberg, Zeits. f. Physik **31**, 681 (1925).
22. G. Landsberg and L. Mandelstam, Compt. rendus **187**, 108 (1928).
23. J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).
24. A. Smekal, Naturwiss. **11**, 873 (1923).
25. R. W. Wood, Phys. Rev. **38**, 2168 (1931).
26. H. H. Voge, J. Chem. Phys. **2**, 264 (1934).

MARCH, 1937 JOURNAL OF CHEMICAL PHYSICS VOLUME 5

Note on the Spectra of the Disubstituted Acetylenes and of the Mustard Oils

Richard M. Badger
Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California
(Received December 22, 1936)

It has been observed that in the Raman spectra of many disubstituted acetylenes the line corresponding to the so-called C≡C frequency is split into two components of not greatly different intensity,[1] though this is not the case in the monosubstituted compounds. In the mustard oils the C≡N Raman line is double,[2] and in allyl mustard oil,[3] the one substance which appears to have been studied with sufficient dispersion, the corresponding infrared band shows definite indications of splitting into two components. This doubling is not observed in the organic thiocyanates. These facts have caused some speculation but so far appear never to have received a satisfactory explanation. The presence of two funda-

[1] For references see J. H. Hibben, Chem. Rev. **18**, 1 (1936).
[2] For references see K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Springer, Berlin, 1931).
[3] W. W. Coblentz, *Investigations of Infra-Red Spectra* (Carnegie Institution, 1905).

mentals in the 2200 cm^{-1} region appears quite impossible for most of the molecules showing the doubling, and on the other hand the coexistence of two forms of molecule with slightly different frequencies appears unlikely, especially in the case of the acetylenes. Consequently the author proposes an explanation involving a Fermi resonance interaction between the C≡C or C≡N fundamental, as the case may be, and the overtone of a certain other vibration of approximately one-half or one-third the frequency.

The situation appears especially clear in the case of the acetylenes. When in acetylene one of the hydrogen atoms is replaced by a heavier atom the C≡C frequency will be considerably increased, even though the triple bond force constant is unaffected. The replacement of the second hydrogen will produce a further increase of about the same amount. A similar situation is to be expected if replacement is by alkyl radicals. Owing to the zigzag structure of these (bond angles around 109° 28′) and the absence of disturbing frequencies the C−C≡C−H or C−C≡C−C groups are able to perform the 2200 cm^{-1} oscillation with very little interaction with the remainder of the molecule. In going from acetylene to the monosubstituted compounds the shift in C≡C frequency is about 160 cm^{-1}. Disubstitution produces a further increase of 150 cm^{-1}, if we measure to the *mean* of the doublet, apparently bringing the frequency close to a multiple of that of another vibration. The shifts observed are not greatly different from those calculated for free C−C≡C−H and C−C≡C−C groups on the assumption of reasonable force constants.

We are now concerned with the identification of the vibration which in a harmonic is capable of interacting with the fundamental of the C≡C oscillation of the disubstituted acetylenes. It must be a vibration which persists, little modified in type and frequency, through all these compounds, beginning with dimethyl acetylene. It must involve the C−C≡C−C group to a very considerable extent, and its frequency must be approximately equal to some submultiple of 2271 cm^{-1}, which is approximately that to be expected for the C≡C fundamental in the absence of the interaction under consideration. There appear to be three possibilities. Two of these are vibrations within the C−C≡C−C group itself which might be designated as C−C oscillations, since they mainly involve the stretching and compression of carbon, carbon single bonds. In the symmetrical motion the frequency should be much lower than that of the C−C vibration in ethane. A rough estimate indicates that it should be around 700 cm^{-1}, and it may be noted that a Raman line occurs at 773 cm^{-1} in dimethyl acetylene. In the unsymmetrical motion, in which the two central atoms of the group move in one direction and the two extreme ones in the opposite direction, the frequency should be well above 1000 cm^{-1}, owing to the very considerable interaction between first and third, and second and fourth atoms in the chain. This vibration should be inactive in the Raman effect but would probably appear strongly in the infrared.

The two vibrations mentioned meet the symmetry requirements and would appear to have roughly the right frequencies for interaction with the 2271 cm^{-1} fundamental in their second and first overtones, respectively. An infrared investigation would settle most simply the question as to which is really the one involved, by establishing the frequency of the latter one. However, it should be noted that in some cases of substitution by other than alkyl radicals the C≡C Raman line appears with three components, suggesting that in some compounds both may play some part. The resonance interaction phenomenon is of course a rather delicate affair, depending as it does upon nearly exact integral ratios between frequencies, and it is rather remarkable that conditions may be satisfied through the considerable series of acetylenes which has been studied.

A third but somewhat less likely possibility should be mentioned, namely a vibration involving a swinging of the hydrogens attached to the extreme carbon atoms of the C−C≡C−C group. In dimethyl acetylene there is one such vibration which would nearly meet the requirements. It is degenerate, inactive in the infrared, and should have a frequency a little above 1000 cm^{-1}. It is one which might roughly be described as a tilting of the two methyl groups away from the symmetry axis, in opposite directions. However, in all other members of the disubstituted acetylene series this oscillation is greatly modified, not

only in nature but presumably also in frequency.

Now in the mustard oils there appears to be a characteristic frequency around 1070 cm^{-1}, about half of the C≡N frequency which in this case is approximately 2150 cm^{-1}. This appears as a strong Raman line in the ethyl and isobutyl compounds and as an intense infrared band in the methyl and ethyl derivatives. The Raman line was not reported for allyl mustard oil but the spectrum appears to have been very weak and incompletely developed. Unfortunately infrared data on this region are also lacking. The Raman line was also apparently missing in phenyl and *p*-tolyl mustard oils but in the former a strong infrared band was found at about 1070 cm^{-1} and in the latter no data are available. In methyl and ethyl thiocyanate, which show no splitting of the C≡N line, the 1070 cm^{-1} Raman line is missing.

It seems rather probable that this frequency which is characteristic of the mustard oils is to be attributed to a C−N vibration. Owing to the asymmetry of the C−N≡C−S group it is permitted to appear in both infrared and Raman spectra.

MARCH, 1937 JOURNAL OF CHEMICAL PHYSICS VOLUME 5

The Dissociation Pressure of a Solid Under Inert Gas Pressure[1]

ALFRED J. PERKINS
Flint, Michigan

(Received November 30, 1936)

The mole fraction of ammonia in equilibrium with barium chloride octammine at 32°C and at various pressures of helium, argon and nitrogen has been determined. At every pressure, the mole fraction is greater than that expected by a simple application of the Poynting relation. An equation has been derived for the chemical potential of a component of a gaseous mixture in terms of the total pressure, the mole fraction, and the second virial coefficients. This equation has been tested and shown to give fair agreement between calculated and observed values. One advantage is the fact that it can be used to calculate the mole fraction of the component of a gas mixture which arises from the dissociation of a solid with which the mixture is in equilibrium. It is also shown how these measurements might be used to calculate the second virial coefficients of gaseous mixtures.

INTRODUCTION

FOR the calculation of equilibria in systems containing one component in two phases, that is, in both the gaseous and solid states, it is necessary to know the vapor pressure of that component over the solid. The way in which the vapor pressure changes with the total pressure is also of great importance. It is well known that increasing the pressure on a solid increases its vapor pressure and that from thermodynamic formulae we may get a quantitative measure of this increase.

At constant temperature, the change of the Gibbs free energy of a system with a change in pressure is given by the relation

$$(\partial G/\partial P)_T = V. \tag{1}$$

When mixtures are to be discussed it is much more convenient to use the chemical potential or partial molal free energy as a measure of the state of any component. The chemical potential of the component i is defined as

$$\mu_i = (\partial F/\partial n_i)_{T,\, V,\, n_k} = (\partial G/\partial n_i)_{T,\, P,\, n_k} \tag{2}$$

and the change of u_i with pressure is given by

$$(\partial \mu_i/\partial P)_T = \bar{v}_i, \tag{3}$$

where $\bar{v}_i$ is the partial molal volume of the component i. The condition that the same substance be in equilibrium between two phases at the same temperature but at different pressures is

$$d\mu_i^1 = d\mu_i^2, \quad \text{or} \quad \bar{v}_i^1 dP^1 = \bar{v}_i^2 dP^2, \tag{4}$$

where superscripts refer to the phase and subscripts refer to the component. This relation was first derived by Poynting[2] for the case of a pure substance in two phases, in which case the

[1] This article is based upon the dissertation submitted to the Faculty of Philosophy of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Poynting, Phil. Mag. (5) **12**, 32 (1881).

chemical potentials become the molal free energies of each phase and the partial molal volumes are the molal volumes.

The effect of pressure on the vapor pressure of liquids has been studied by several investigators.[3-6] In all cases the experimental increase in vapor pressure was greatly in excess of that calculated by a simple application of Poynting's equation in the integrated form, assuming that the volume of the liquid phase remains constant and using total volume in place of partial molal volume for the gas phase. For example, Bartlett[4] found a fourfold increase above the calculated value for water compressed by nitrogen at 1000 atmospheres. Van Laar[7] using Bartlett's data demonstrated that his complex equation of state for gas mixtures in equilibrium with a condensed phase was able to predict the effect of a compressed gas upon the vapor pressure of water.

TABLE I.

P	X_2	PX_2	log PX_2
A. WITH HELIUM			
3.809	1.000	3.809	.58081
3.810	1.000	3.810	.58092
12.711	.3023	3.882	.58900
13.363	.2907	3.884	.58930
37.94	.1046	3.969	.59863
42.52	.0937	3.984	.60032
52.07	.0775	4.035	.60584
57.47	.0704	4.046	.60703
B. WITH ARGON			
12.807	.3165	4.053	.60778
34.12	.1250	4.265	.62992
41.26	.1086	4.481	.65137
54.17	.0840	4.550	.65801
54.77	.0832	4.558	.65877
C. WITH NITROGEN			
33.70	.1238	4.172	.62034
34.12	.1234	4.213	.62459
D. WITH HYDROGEN			
22.36	.1745	3.901	.5912

[3] Larson and Black, J. Am. Chem. Soc. **47**, 1015 (1925).
[4] Bartlett, J. Am. Chem. Soc. **49**, 65 (1927).
[5] Pollitzer and Strebel, Zeits. f. physik. Chemie **110**, 768 (1924).
[6] Saddington and Krase, J. Am. Chem. Soc. **56**, 353 (1934).
[7] J. J. Van Laar, Zeits. f. physik. Chemie **A145**, 207 (1929).

Because of the complexity of the treatment necessary for the calculation of the vapor pressure of solutions, a much simpler case is that of a dissociating solid. McHaffie[8] studied the system sodium sulfate-sodium sulfate decahydrate-water vapor under air pressure up to 100 atmospheres. He obtained negative as well as positive deviations from the calculated values. Braune and Strassman[9] determined the vapor pressure of iodine in carbon dioxide with total pressures as high as fifty atmospheres. The system used in this investigation was barium chloride-barium chloride octammine-ammonia, which has been the subject of two previous studies.[10, 11] Lurie and Gillespie,[10] working at 45°C, used nitrogen as the compressing gas and covered the pressure range from the vapor pressure of the pure ammine to a total pressure of sixty atmospheres. Field[11] used both mechanical and inert gas pressure, hydrogen being the compressing gas in the majority of his

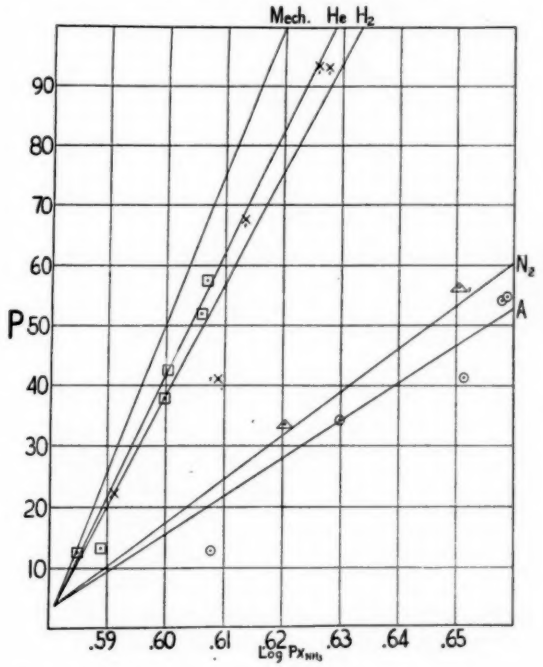


FIG. 1. Results with helium——□; results with argon ——○; results with nitrogen——△; Field's nitrogen results——△$_F$; result with hydrogen——×; Field's hydrogen results——×$_F$.

[8] McHaffie, Phil. Mag. (7) **1**, 561 (1926).
[9] Braune and Strassman, Zeits. f. physik. Chemie **A143**, 225 (1929).
[10] Lurie and Gillespie, J. Am. Chem. Soc. **49**, 1146 (1927).
[11] T. E. Field, J. Am. Chem. Soc. **56**, 2535 (1934).

measurements. He also made several measurements with nitrogen. Inasmuch as the magnitude of the discrepancy between the observed vapor pressures and those calculated by Ponyting's equation depends upon the nature of the compressing gas, it was thought that measurements using several other gases as the compressing agent might prove to be of interest. The two monatomic gases, helium and argon, were used with pressures ranging from the vapor pressure of the pure ammine up to a total pressure of 58 atmospheres.

Experimental

The anhydrous barium chloride was made by heating the C.P. dihydrate, crushing the resulting mass and reheating over a low gas flame. Ammonia was taken from a tank of the anhydrous liquid. The various compressing gases were used as obtained from commercial sources.

The method and apparatus is fully described by Field.[11] The only change made in the design of the apparatus was in the construction of the high pressure manometers. Instead of using a tube made from two capillaries of different bore, two small bulbs were blown near the top of the manometers. When carefully made, they withstood the highest pressure reached. Besides helium and argon, hydrogen and nitrogen were used in the preliminary experiments. The entire apparatus was enclosed in an air thermostat held at 32°C±.05.

Results

The results are given in Table I, where P is the total pressure in atmospheres, X_2 is the mole fraction of ammonia and PX_2 is the Dalton partial pressure of ammonia.

These results are plotted in Fig. 1 along with those of Field for hydrogen and nitrogen. The curves drawn are those given by the method of least squares. The curve labeled mechanical is taken from Field's measurements with mechanical pressure.

Discussion

The curves in Fig. 1 show that the Dalton partial pressure does not reproduce the true state of affairs in gas mixtures. This is to be expected since Dalton's law applies only to perfect gases. The quantities to be compared are the chemical potential of ammonia in the gas mixture at a total pressure P and the chemical potential of pure ammonia at a pressure given by the ammine when under the mechanical pressure P. Before calculating the chemical potential of a component of a gas mixture, an expression for the free energy of that mixture must first be obtained. Statistical mechanics gives for the Helmholtz free energy,

$$F=\sum_i n_i F_i^0(T)+\sum_i n_i RT \log n_1/V - NRT \sum_{ik} \frac{B_{ik} n_i n_k}{\sigma_{ik} V}, \quad (5)$$

where n_i is the number of moles of component i, $F_i^0(T)$ is the part of the free energy of component i which depends only on the temperature and is the free energy of that component in the pure state at unit value of n/V. V is the volume, σ_{ik} is a symmetry number which is unity except when $i=k$, in which case it is equal to two, and B_{ik} is given by,

$$B_{ik}=\int_0^\infty (e^{-U_{ik}/kT}-1)4\pi r^2 dr. \quad (6)$$

This equation is taken from Guggenheim.[12] Here U_{ik} is the potential energy between the pair of molecules i and k as a function of r, the distance between them. A derivation and discussion for the case of a single gas is given in Slater and Frank.[13] The calculation of the B_{ik}'s will be given later.

From Eq. (5) and the definition of the chemical potential as given in the introduction, we get,

$$\mu_i=F_i^0(T)+RT+RT \log n_i/V - NRT\sum_k B_{ik} n_k/V. \quad (7)$$

This can be written as

$$(\mu_i-\mu_i^0)/RT=\log n_i/V-N\sum_k B_{ik} n_k/V, \quad (8)$$

where $u_i^0=F_i^0(T)+RT$, and is a function of the

[12] Guggenheim, *Modern Thermodynamics* (Methuen Co., London), pp. 73.

[13] Slater and Frank, *Introduction to Theoretical Physics* (McGraw-Hill Book Co., N. Y.), pp. 462.

TABLE II.

Gas	b cc/mole	a cc² atmos./mole	E erg/molecule	B_1 cc/mole	B_2 cc/mole	B_{12} cc/mole
Argon	32.19	1.345×10^{6}	2.7014×10^{-14}	0.711×10^{-22}		1.915×10^{-22}
Helium	23.70	.0341	3.875	−0.737		−0.527
Nitrogen	39.13	1.390	2.7082	0.540		1.854
Hydrogen	26.61	.244	2.3074	−0.556		00.275
Ammonia	37.07	4.170	1.7946		4.272×10^{-22}	

temperature alone. This equation gives the chemical potential in terms of the concentration of the gases. However, in the experiments, the measured quantities were the total pressure and the mole fractions of the components, and therefore the chemical potential must be expressed in terms of those quantities. Using Eq. (5) again, we can get an expression relating total pressure and the composition, i.e.,

$$P=-(\partial F/\partial V)_{T,\,n}=\sum n_iRT/V - NRT\sum_{ik}\frac{B_{ik}n_in_k}{\sigma_{ik}V^2}. \quad (9)$$

Since this is a two component system, there is also the condition

$$n_1/V=(X_1/X_2)(n_2/V), \quad (10)$$

where subscript 1 refers to the inert gas and the subscript 2 to the ammonia. Combining (9) and (10) and solving for (n_2/V) gives

$$n_2/V=PX_2/RT(1+DPX_2^2/(RT)^2+\ +), \quad (11)$$

where

$$D=RT[(X_1/X_2)^2NB_1/2+NB_2/2 +NB_{12}(X_1/X_2)]. \quad (12)$$

Use of higher terms in the expansion would be unjustified since only the second virial coefficient was taken in (9).

Putting this value for n_2/V into Eq. (8) we get

$$M=(u_2-u_2^0)/RT=\log PX_2/RT\ . +P/RT[(NB_1/2-NB_{12}+NB_2/2) \times(1-X_2)^2-NB_2/2]. \quad (13)$$

In order to use this relation it is necessary to get values for the B's by evaluating the integral of Eq. (6). To do this two assumptions have to be made: first, that the attractive part of U_{ik} is small compared to kT, and second, that the repulsive part varies so rapidly with r that it can be considered zero if r is greater than r_0 and infinite if r is less than r_0. The integral then becomes

$$B_{ik}=-4\pi r_0^3/3+1/kT\int_{r_0}^{\infty}4\pi r^2U_{ik}dr, \quad (14)$$

the exponential being expanded in a power series and terms after the first dropped. London and Eisenschitz[14] have shown that U_{ik} is approximately of the form

$$U_{ik}=3/2(1/r^6)\alpha_i\alpha_k\Delta E_i\Delta E_k/(\Delta E_i+\Delta E_k), \quad (15)$$

where the α's are the polarizabilities of the molecules i and k, and ΔE_i and ΔE_k are approximately their ionization potentials. Substituting into Eq. (14) and integrating gives

$$B_{ik}=-4\pi r_0^3/3+4\pi/3kT\,A_{ik}/r_0^3, \quad (16)$$

where $A_{ik}=3/2\alpha_i\alpha_k\Delta E_i\Delta E_k/(\Delta E_i+\Delta E_k)$. (17)

Returning now to Eq. (9) for the pressure of a gas mixture, we see that for a pure gas it can be put into the form

$$PV/RT=1-NB/2V. \quad (18)$$

Comparing this with Eq. (16) we see that $NB/2$ can be written as

$$NB=-b+a/RT, \quad (19)$$

where $b=2\pi Nr_0^3/3$; $a=2\pi N^2A/3r_0^3$. (20)

The two quantities a and b may be identified with the constants in van der Waals' equation of

[14] London and Eisenschitz, Zeits. f. Physik **60**, 491 (1930).

state for gases. Thus we have a means of calculating the radii of the molecules of a gas and the forces between those molecules.

This result may be used in the following manner to calculate approximately the B for a pair of unlike molecules, assuming that for the distance between their centers at a collision we may take the sum of their individual radii. The individual radii are calculated from van der Waals' b constant. This result is then used with the a constant to get a value of A for the pure gas. These constants were taken from Landolt-Börnstein.[15] In the case of a perfect gas Eq. (17) reduces to $A=3/2\alpha^2\Delta E/2$. Values for the polarizability can be obtained from this by substituting in it the values of A just found and the values of ΔE from the dispersion formula of the gas. These values of the α's and the ΔE's can then be used in Eq. (17) to obtain the A's between unlike molecules. From these values of the A_{ik}'s and the sum of the individual radii, we can calculate the B_{ik}'s using Eq. (16).

In Table II are tabulated the values of van der Waals' a and b used, the values of ΔE used, and the values of B_1, B_2 and B_{12} calculated therefrom.

TABLE III.

P	M	$M-M_{mech}$	X_2 OBS.	X_2 CAL.
		A. WITH HELIUM		
12.711	−8.8148	−0.0112	.3023	.3056
13.363	−8.8042	−0.0012	.2907	.2917
37.94	−8.7786	+0.0019	.1046	.1044
42.52	−8.7734	+0.0026	.0937	.0934
42.62	−8.7861	−0.0103	.0922	.0932
52.07	−8.7575	+0.0096	.0775	.0767
57.47	−8.7545	+0.0075	.0704	.0697
		B. WITH ARGON		
12.81	−8.7880	+0.0155	.3165	.3115
34.12	−8.8190	−0.0352	.1250	.1295
41.26	−8.7974	−0.0203	.1086	.1109
54.17	−8.8310	−0.0658	.0840	.0897
54.77	−8.8322	−0.0676	.0832	.0890
		C. WITH NITROGEN		
33.70	−8.8407	−0.0566	.1238	.1297
34.12	−8.8334	−0.0496	.1234	.1290
56.68	−8.8560	−0.0932	.0793	.0869
55.97	−8.8516	−0.0881	.0804	.0877

[15] Landolt-Börnstein, *Tabellen*, HwI (Springer, Berlin), pp. 253.

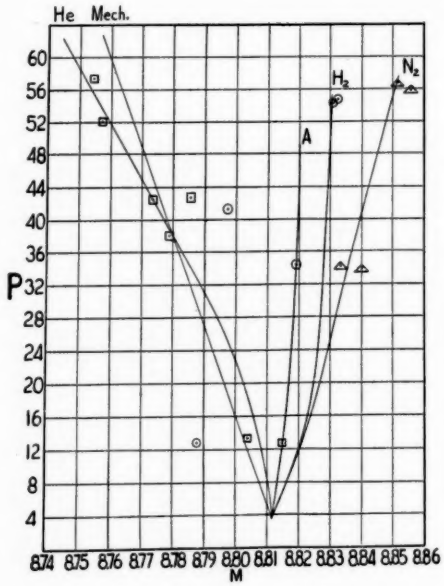


FIG. 2. Helium———□; argon———○; nitrogen———△.

From the experimental results and the values of the B's given in Table II, the values of the function $M=(\mu_2-\mu_2^0)/RT$ have been calculated. Eq. (13) has also been used to predict the mole fraction of ammonia in the gas mixture at a total pressure P, the M used being that of pure ammonia at a pressure of the ammine under mechanical pressure P. These values are given in Table III.

These values of M have been plotted in Fig. 2 along with the curve for the value of the function M at a mechanical pressure P. The curves given in Fig. 2 for the various gases were obtained by making calculations of M from points on the curves of Fig. 1.

The agreement between the mechanical pressure curve and the curve for helium is quite good, the deviation being about 0.1 percent. This would mean a discrepancy of about 1 percent in the dissociation pressure of the ammine under mechanical pressure. For the other three gases the deviations are large and from them one would get a dissociation pressure less than the normal vapor pressure of the ammine. The calculation of the mole fraction of ammonia present gives in general a larger value than that observed. The greatest deviation

TABLE IV.

MIXTURE	B_{12} THEO.	B_{12} OBS.
Argon Ammonia	1.915×10^{-22}	1.379×10^{-22}
Nitrogen Ammonia	1.854	1.076
Hydrogen Ammonia	0.275	−0.347

is with nitrogen at 56 atmospheres, where it is 9 percent.

The reverse calculation has been carried out. That is, the values for the constant B_{12} which would give agreement between the respective gas pressure and mechanical pressure curves were calculated. They are given in Table IV as B_{12} obs. If it is assumed that the values of A_{12} are correct and that the blame might be laid to the fact that one cannot add the individual radii of unlike molecules to get the collision diameter between them, one finds that a small increase in the collision diameter for unlike molecules will account for the discrepancy. For argon ammonia, the collision diameter must be increased by 4.3 percent. For nitrogen ammonia, the increase calculated is 0.198×10^{-8} cm, or 5.6 percent. The collision diameter for the calculation of B_{12} for hydrogen ammonia mixtures has to be altered the largest amount, an increase of 8.5 percent being necessary. The reason that such a small change in the collision diameter has such a large effect on the value of B_{12} is due to the fact that B_{12} is given by the difference of two terms, one of which is directly proportional to the cube of the collision diameter and the other inversely proportional to the cube of the diameter.

As a check on the results obtained here for nitrogen ammonia mixtures and on the application of the method of calculation, the experimental results of Lurie and Gillespie[10] have been used in a similar calculation using the observed value of B_{12}. The results of these calculations are given in Table V, where P is the total experimental gas pressure at which Lurie and Gillespie measured the equilibrium mole fraction X_2 obs. M is the characteristic function of ammonia over the ammine under the experimental conditions, calculated from Lurie and Gillespie's mole fractions and using our B_{12}. $M-M_{\text{mech}}$ is the difference between the calculated characteristic function and that of pure ammonia over the ammine under the mechanical pressure P. Finally X_2 cal. (which should be identical with X_2 obs.) is the mole fraction of the ammonia one would expect with a total gas pressure P. The agreement between the calculated and the true values is quite good considering the approximations which have to be made.

TABLE V.

P	M	$M-M_{\text{mech}}$	X_2 OBS.	X_2 CAL.	%
7.123	−8.2415	0.0000	1.000	1.000	
10.133	−8.2514	−0.0125	.7040	.7062	+0.3
11.716	−8.2080	+0.0295	.6393	.6204	−2.9
13.272	−8.2103	+0.0258	.5655	.5734	−1.4
23.695	−8.1902	+0.0381	.3313	.3186	−3.8
32.818	−8.1740	+0.0470	.2478	.2360	−4.8
47.912	−8.1762	+0.0331	.1743	.1682	−3.5
60.864	−8.1244	+0.0747	.1484	.1372	−7.5

Acknowledgment.—The author wishes to thank Professor J. C. W. Frazer for his continued advice and encouragement, also, Dr. J. H. Frazer and Dr. J. E. Mayer for their assistance with the theoretical problem. Special thanks are due to Dr. T. E. Field who kindly lent the pressure block around which the apparatus was built.

Theory of the Electronic Energy Levels of Simple Hydrides

J. R. STEHN
Department of Physics, University of Wisconsin, Madison, Wisconsin
(Received January 13, 1937)

The conventional extremely simplified form of the Heitler-London theory is applied to the energy levels of the molecules BH, CH, NH, OH, FH. The exchange integrals, determined empirically to make the theory fit the known levels, are found to vary slowly and regularly from one molecule to the next. The energies of states as yet unobserved are predicted.

INTRODUCTION

VAN VLECK and Sherman[1] have discussed the many reasons why the molecular theory of Heitler, London, Slater and Pauling, should not be accurate, especially in the simplified form in which it is commonly applied. Yet, as they also point out, it is just that simplified form which has enjoyed the most success. The present work constitutes further evidence of its effectiveness, in a group of molecules as yet untried, *viz.* in hydrides of the type XH, where X represents an element of the first row of the periodic table: B, C, N, O or F. The work is also of use in calculations on certain more complicated molecules, such as CH_4 and H_2O.[2] The simplified HLSP theory calculates the energy of a polyatomic molecule in terms of the energy parameters characteristic of pairs of atoms in the molecule, and the energy parameters for the pairs XH are of course found here.

By proper choice of atomic orbitals, one should be able to calculate the values of these parameters. But a less laborious (and, for our purposes, more accurate) method of evaluation is the empirical one. The parameters are so chosen as to make the theoretical energy expressions most nearly represent the known energy levels of the molecules XH.

THEORETICAL ENERGY EXPRESSIONS

We consider XH as being formed from atom X in its normal configuration $1s^22s^22p^n$ plus atom H in the configuration $1s$. The $2p$ orbits of X for $\lambda=0$, 1, and -1, and the $1s$ orbit of H are denoted, respectively, by σ, π_+, π_-, and H. The $1s$ and $2s$ orbits of X are given no special symbols, for in our approximation the energy contributions of these orbits are identical for the various states of a given molecule and can therefore be combined with the "Coulomb" terms. A typical molecular configuration is then $\sigma^2\pi_+H$, which happens to represent a Π state of NH.

We assume that:

(1) All configurations other than those of the type just described can be neglected.[3] Thus we do not consider the perturbing effects of ionic configurations, such as $1s^22s^22p^{n+1}$, in which all the electrons are effectively attached to the X nucleus. Nor do we consider configurations in which one of the electrons of X is excited, e.g., $1s^22s2p^{n+1}H$. In addition, we neglect interactions among those configurations which are considered (e.g., in NH, $\sigma^2\pi_+H$ and $\pi_+{}^2\pi_-H$).

(2) All orbitals are orthogonal to one another.[4]

(3) The magnitude of an "exchange integral" (defined below) is roughly proportional to the amount of "overlapping" of the orbits concerned in the exchange. Therefore $|J_{\sigma H}| \gg |J_{\pi H}|$.

(4) Coulomb terms are nondirectional; that is, $K_{\sigma H}=K_{\pi H}$.

(5) The states of a given molecule have the same equilibrium separation, r_e, so that the parameters (Coulomb and exchange integrals)

[1] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935). This admirable summary article should be consulted on questions concerning the terminology and underlying philosophy of the work.

[2] H_2O—J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933). H_2O_2, N_2H_4—W. G. Penney and G. B. B. M. Sutherland, J. Chem. Phys. **2**, 492 (1934). CH_4—J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934). CH_2, CH_3, CH_4—H. H. Voge, J. Chem. Phys. **4**, 581 (1936).

[3] This assumption is based mainly on energy considerations. It appears to be invalid for FH, where, in agreement with standard chemical ideas, ionic configurations are probably important.

[4] Values of their S integrals by C. E. Ireland, Phys. Rev. **43**, 329 (1933), and by W. H. Furry and J. H. Bartlett, Jr., Phys. Rev. **39**, 210 (1932), show how invalid this assumption really is. A far-reaching discussion of the effects of nonorthogonality is given by A. S. Coolidge and H. M. James, J. Chem. Phys. **2**, 811 (1934).

have identical values for all the states of a given molecule. Calculations for repulsive states refer only to this same separation, of course—similarly with applications of the parameters to polyatomic molecules. Fortunately, the molecules considered here conform fairly well to this assumption. Note that r_e values for different molecules need not be equal.

These assumptions are roughly analogous to those made by Eyring and his colleagues in their extensive activation energy calculations.[5] Here, however, we take into account the directional properties of the orbitals, as well as the internal energy of the X atom, and we thus ought to obtain more accurate results.

The Dirac vector model, as used by Van Vleck[6] and Serber,[7] offers perhaps the most elegant method of deriving the energy expressions. On the basis of assumptions (1) and (2) above, we need merely the fundamental formula for the Hamiltonian matrix:[8]

$$\mathfrak{H}=\sum_{\text{all pairs}} K_{ij}-\sum_{i,\,\mu} J_{i\mu}-2\sum_{\mu>\nu} J_{\mu\nu} -\sum_{i>j}\tfrac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)J_{ij}$$

K_{ij} and J_{ij} are, respectively, the Coulomb and exchange integrals between orbits i and j:

$$K_{ij}\equiv\int\int\psi_i^*(1)\psi_j^*(2)\mathfrak{H}\psi_i(1)\psi_j(2)d\tau_1 d\tau_2,$$

$$J_{ij}\equiv\int\int\psi_j^*(1)\psi_i^*(2)\mathfrak{H}\psi_i(1)\psi_j(2)d\tau_1 d\tau_2.$$

The Roman and Greek subscripts on the J's refer, respectively, to "free" and to "filled" orbits, i.e., to those which appear once and to those which appear twice in the configuration. The $\mathbf{s}_i$ are vector spin matrices.

To determine the characteristic values of $\mathfrak{H}$, we need those of $\sum[-\frac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)J_{ij}]$. These are, for the cases in which we are interested, and for various values of the total spin, S:

2 free electrons:

$S=1$: $-J_{12}$
$S=0$: $+J_{12}$

3 free electrons:

$S=\frac{3}{2}$: $-J_{12}-J_{13}-J_{23}$
$S=\frac{1}{2}$: $\pm 2^{-\frac{1}{2}}[(J_{12}-J_{13})^2+(J_{12}-J_{23})^2+(J_{13}-J_{23})^2]^{\frac{1}{2}}$

4 free electrons, with $J_{13}=J_{23}$, $J_{14}=J_{24}$:

$S=2$, $S_{12}=1$: $-J_{12}-J_{34}-2J_{13}-2J_{14}$
$S=1$, $S_{12}=1$: $-J_{12}-\frac{1}{2}J_{13}-\frac{1}{2}J_{14}$ $\pm[(J_{34}-\frac{1}{2}J_{13}-\frac{1}{2}J_{14})^2+2(J_{13}-J_{14})^2]^{\frac{1}{2}}$
$S=1$, $S_{12}=0$: $+J_{12}-J_{34}-J_{13}-J_{14}$
$S=0$, $S_{12}=1$: $-J_{12}-J_{34}+J_{13}+J_{14}$
$S=0$, $S_{12}=0$: $+J_{12}+J_{34}-J_{13}-J_{14}$

The formulas for the cases of 2 and 3 free electrons are well known.[1] Those for the 4 electron case, on the assumption made above that two pairs of J's are equal, can be readily worked out by a variant of Goudsmit's inspection method,[9] since this assumption reduces the problem to that of three vectors, $\mathbf{s}_3$, $\mathbf{s}_4$ and $\mathbf{S}_{12}$ ($\equiv\mathbf{s}_1+\mathbf{s}_2$). It is also possible to obtain these results from the work of Johnson,[10] Schlapp,[11] or especially of Merrill[12] on more general 4 vector problems. The explicit permutation matrices given by Serber[13] offer still another way of deriving these formulas.

The only 4-free-electron problem we consider is that of the $\pi_+\pi_-\sigma$ $^2\Pi$ configuration of NH. From obvious symmetry considerations, $J_{\sigma\pi_+}=J_{\sigma\pi_-}$, and $J_{H\pi_+}=J_{H\pi_-}$; that is why the characteristic

TABLE I. *BH.* ($K=-1.36$, $J_\pi=+0.62$, $J_\sigma=-2.23$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma H\ ^3\Sigma^+$	$^2P+K_\sigma-J_\sigma$	$^2P+0.87=+0.87$	
$\pi H\ ^1\Pi$	$^2P+K_\pi+J_\pi$	$^2P-0.74=-0.74^*$	-0.74
$\pi H\ ^3\Pi$	$^2P+K_\pi-J_\pi$	$^2P-1.98=-1.98$	
$\sigma H\ ^1\Sigma^+$	$^2P+K_\sigma+J_\sigma$	$^2P-3.59=-3.59^*$	-3.59

[5] See, for example, A. Sherman and H. Eyring, J. Am. Chem. Soc. **54**, 2661 (1932).
[6] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).
[7] R. Serber, Phys. Rev. **45**, 461 (1934) and J. Chem. Phys. **2**, 697 (1934).
[8] Reference 6, Eq. (7). The use of J and K there is the opposite of that here.

[9] S. Goudsmit, Phys. Rev. **35**, 1325 (1930). The method is also illustrated on p. 226 of reference 1.
[10] M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).
[11] R. Schlapp, Proc. Roy. Soc. Edinburgh **54**, 109 (1934).
[12] R. A. Merrill, Phys. Rev. **46**, 487 (1934). Merrill's vectors $\mathbf{L}$, $\mathbf{S}_d$, $\mathbf{J}_d$, $\mathbf{s}_m$, $\mathbf{s}_n$, $\boldsymbol{\sigma}$, $\mathbf{J}$, correspond to our $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{S}_{12}$, $\mathbf{s}_3$, $\mathbf{s}_4$, $\mathbf{S}_{34}$, $\mathbf{S}$. His matrices do not give the $\mathbf{s}_1\cdot\mathbf{s}_3$ and $\mathbf{s}_1\cdot\mathbf{s}_4$ interactions; but these can be found in our case, where $s_1=s_2=\frac{1}{2}$, by observing that $\mathbf{s}_1\cdot\mathbf{s}_3=\mathbf{s}_2\cdot\mathbf{s}_3$ if $\mathbf{s}_1$ and $\mathbf{s}_2$ are parallel ($S_{12}=1$) and that $\mathbf{s}_1\cdot\mathbf{s}_3=-\mathbf{s}_2\cdot\mathbf{s}_3$ if $\mathbf{s}_1$ and $\mathbf{s}_2$ are antiparallel ($S_{12}=0$). Formulas are also given for the 3 vector problem which we would have if we let $J_{34}=0$; these should allow a check in one limiting case. However, there is a slight error in Merrill's 3 vector formulas (2) on p. 488; the quantity $\frac{1}{2}B_dS_d$ should be added to each of the first three expressions for W, while $-\frac{1}{2}B_d(S_d+1)$ should be added to the last expression for W. This error in no way affects the remaining results of Merrill's paper, as it merely introduces an additive constant which cancels out in all his applications.
[13] R. Serber, J. Chem. Phys. **2**, 697 (1934).

TABLE II. *CH*. ($K=-1.79$, $J_\pi=+0.80$, $J_\sigma=-2.27$, $3F_2=+0.55$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma^2\ H\ ^2\Sigma^+$	$^1S-6F_2\quad+2K_\sigma\quad-J_\sigma$	$^1S-0.62=+2.04$	
$\pi\sigma\ H\ ^2\Pi$	$^1D-\frac{3}{2}F_2+K_\pi+K_\sigma+\frac{1}{2}J_\pi-J_\sigma$	$^1D+0.60=+1.85$	
$\pi_+\pi_-\ H\ ^2\Sigma^+$	$^1D+6F_2+2K_\pi\quad-J_\pi$	$^1D-1.49=-0.24$	-0.25
$\pi\sigma\ H\ ^4\Pi$	$^3P\quad+K_\pi+K_\sigma-J_\pi-J_\sigma$	$^3P-0.32=-0.32$	
$\pi_+\pi_-\ H\ ^2\Sigma^-$	$^3P\quad+2K_\pi\quad+J_\pi$	$^3P-0.99=-0.99^*$	-0.99
$\pi_+^2\ H\ ^2\Delta$	$^1D\quad+2K_\pi\quad-J_\pi$	$^1D-2.59=-1.34^*$	-1.33
$\pi_+\pi_-\ H\ ^4\Sigma^-$	$^3P\quad+2K_\pi\quad-2J_\pi$	$^3P-3.39=-3.39$	
$\pi\sigma\ H\ ^2\Pi$	$^3P+\frac{3}{2}F_2+K_\pi+K_\sigma-\frac{1}{2}J_\pi+J_\sigma$	$^3P-4.18=-4.18^*$	-4.18

TABLE III. *NH*. ($K=-2.01$, $J_\pi=+0.90$, $J_\sigma=-2.20$, $3F_2=+0.69$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma^2\pi_+\ H\ ^1\Pi$	$^2P-3F_2+K_\pi+2K_\sigma+J_\pi-J_\sigma$	$^2P+0.40=+3.95$	
$\pi_+\pi_-\sigma\ H\ ^1\Sigma^-$	$^2D\quad+2K_\pi+K_\sigma+J_\pi-J_\sigma$	$^2D+1.09=+3.46$	
$\pi_+\pi_-\sigma\ H\ ^3\Sigma^+$	$^2P\quad+2K_\pi+K_\sigma-J_\pi-J_\sigma$	$^2P-0.71=+2.84$	
$\sigma^2\pi_+\ H\ ^3\Pi$	$^2P-3F_2+K_\pi+2K_\sigma-J_\pi-J_\sigma$	$^2P-1.40=+2.15$	
$\pi_+\pi_-\sigma\ H\ ^5\Sigma^-$	$^2D-3F_2+2K_\pi+K_\sigma\quad-J_\sigma$	$^2D-0.50=+1.87$	
$\pi_+^2\sigma\ H\ ^3\Delta$	$^2D\quad+2K_\pi+K_\sigma-J_\pi-J_\sigma$	$^2D-0.71=+1.66$	
$\pi_+^2\pi_-\ H\ ^1\Pi$	$^2D+3F_2+3K_\pi$	$^2D-1.32=+1.05^*$	$+1.07$
$\pi_+^2\pi_-\ H\ ^3\Pi$	$^2D+3F_2+3K_\pi\quad-2J_\pi$	$^2D-3.12=-0.75^*$	-0.73
$\pi_+\pi_-\sigma\ H\ ^1\Sigma^+$	$^2P\quad+2K_\pi+K_\sigma-J_\pi+J_\sigma$	$^2P-5.11=-1.56$	-1.66
$\pi_+\pi_-\sigma\ H\ ^5\Sigma^-$	$^4S\quad+2K_\pi+K_\sigma-2J_\pi-J_\sigma$	$^4S-1.61=-1.61$	
$\pi_+^2\sigma\ H\ ^1\Delta$	$^2D\quad+2K_\pi+K_\sigma-J_\pi+J_\sigma$	$^2D-5.11=-2.74^*$	-2.72
$\pi_+\pi_-\sigma\ H\ ^3\Sigma^-$	$^4S+3F_2+2K_\pi+K_\sigma-J_\pi+J_\sigma$	$^4S-4.42=-4.42^*$	-4.40

values were tabulated above only for the restricted 4 electron problem. Furthermore in this problem, as in any other involving a $\pi_+\pi_-$ pair of free electrons, the states are Σ^+ or Σ^- according as $S_{\pi_+\pi_-}$ is 0 or 1.

The atomic J's and K's can be evaluated in terms of the Slater-Condon-Shortley parameters F_0 and F_2:[14]

$$K_{\sigma\sigma}=F_0+4F_2$$

$$J_{\pi\sigma}=3F_2,\qquad K_{\pi\sigma}=F_0-2F_2,$$

$$J_{\pi_+\pi_-}=6F_2,\qquad K_{\pi_+\pi_-}=F_0+F_2.$$

It is convenient to include in the energies of the molecular states the energies of the atomic states into which they dissociate; thus the F_0 terms are eliminated. This is done by means of Slater's formulas[14] for the energies of p^n configurations. For example, the states of the N atom have energies: $^2P=3F_0$, $^2D=3F_0-6F_2$, $^4S=3F_0-15F_2$.

The molecular J's and K's will be abbreviated by omission of the subscript H; thus $J_\sigma\equiv J_{\sigma H}$, etc. In Tables I–V, we have used the fact that $|J_\sigma|$ is larger than the other J's (assumption 3) to expand all the square roots into expressions linear in the J's. This is effectively the approximation of electron pairing. That it is quite a good one here (the maximum resulting error being 0.05 volt) is in large part due to the approximate equality of $J_{\pi H}$ and $J_{\pi\sigma}$.

[14] J. C. Slater, Phys. Rev. **34**, 1293 (1929); E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

DETERMINATION OF PARAMETERS

Although there are explicitly five parameters in the energy expressions, atomic spectra fix the value of one of them, F_2.[15] The remaining four are more than can be determined from the observed molecular energy levels. To simplify matters, and to follow the precedent of many another work on molecular theory, we have arbitrarily chosen K_π equal to K_σ (assumption 4). This makes the Coulomb terms equal for all states of a given molecule. In the case of CH and NH the three parameters remaining, J_π, J_σ, and K (the sum of the Coulomb and inner shell contributions), were determined so as to fit best the four or five observed energy levels. In the case of BH

[15] Actually, as Slater, reference 14, has shown, *two* values of F_2 can be found, depending on which pair of atomic levels (in C, N, and O) is assumed to be given correctly by his theory. We have here used the average of these two values.

and OH, which possess but two observed levels apiece, the three parameters could not be completely specified. Here, then, values of the parameters were chosen which simultaneously fitted the observed pairs of levels and ran smoothly from one hydride to the next. In the case of FH, both J_π and J_σ were extrapolated, while K was chosen to fit the single observed level.

TABLES

All values are in electron volts. Predicted energy values denoted by an asterisk are effectively the ones which were adjusted (by proper choice of parameters) to fit the experimental values. Experimental energy values have been corrected for the zero-point vibrational energy before being tabulated here. They come from the following sources:

BH and CH: from Mulliken.[16]

NH: from the recent compilation of Lunt, Pearse, and Smith.[17] The singlet-triplet separation ($\alpha, \equiv {}^1\Delta - {}^3\Sigma^-$) has been arbitrarily chosen here to fit the theoretical separation. The heat of dissociation of the ${}^3\Sigma^-$ level is Mulliken's estimate.[16]

OH: from Mulliken.[16] Recent work[18] would seem to favor raising the levels about 0.5 volt, but see later discussion of Results (2).

FH: quoted by Pauling.[19]

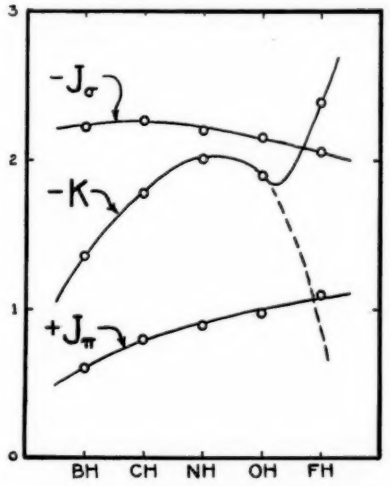


FIG. 1. Values in electron volts of the exchange integrals, J_π and J_σ, and of the total Coulomb terms K, as a function of atomic number. $-J_\pi$ and $-J_\sigma$ are, respectively, Van Vleck's $N_{\pi\pi}$ and $N_{\sigma\sigma}$, reference 2. The dashed curve represents the course the $-K$ curve would presumably take if there were no ionic effect in FH.

[16] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932), Table XVIII.

[17] R. W. Lunt, R. W. B. Pearse, and E. C. W. Smith, Proc. Roy. Soc. **A155**, 173 (1936).

[18] H. Sponer, *Molekülspektren*, Vol. I (1935), p. 27, quotes 4.4 volts as the heat of dissociation of OH. 4.3 volts is the value which would have been obtained (rather than 5.1) by O. Riechemeier, H. Senftleben, and H. Pastorff, Ann. d. Physik **19**, 202 (1934), if they had used in their calculations a reasonably recent value of the heat of dissociation of O_2. This value is found indirectly from their measurements on the energy of dissociation of H_2O into H+OH.

[19] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932). This chemical value agrees even better with the band-spectroscopic estimate of D. E. Kirkpatrick and E. O. Salant, Phys. Rev. **48**, 945 (1935), than does the older chemical value they quote.

TABLE IV. *OH*. ($K=-1.90$, $J_\pi=+0.98$, $J_\sigma=-2.16$, $3F_2=+0.85$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\sigma^2\pi_+\pi_-$ H ${}^2\Sigma^+$	${}^1S-3F_2+2K_\pi+2K_\sigma- J_\pi-J_\sigma$	${}^1S-1.57=+2.58$	
$\pi_+^2\pi_-\sigma$ H ${}^2\Pi$	${}^1D-\frac{3}{2}F_2+3K_\pi+ K_\sigma-\frac{1}{2}J_\pi-J_\sigma$	${}^1D-0.65=+1.29$	
$\sigma^2\pi_+\pi_-$ H ${}^2\Sigma^-$	${}^3P \quad +2K_\pi+2K_\sigma+ J_\pi-J_\sigma$	${}^3P+1.24=+1.24$	
$\sigma^2\pi_+^2$ H ${}^2\Delta$	${}^1D \quad +2K_\pi+2K_\sigma- J_\pi-J_\sigma$	${}^1D-0.72=+1.22$	
$\pi_+^2\pi_-^2$ H ${}^2\Sigma^+$	${}^1D+3F_2+4K_\pi \quad -2J_\pi$	${}^1D-3.01=-1.07^*$	-1.07
$\sigma^2\pi_+\pi_-$ H ${}^4\Sigma^-$	${}^3P \quad +2K_\pi+2K_\sigma-2J_\pi-J_\sigma$	${}^3P-1.70=-1.70$	
$\pi_+^2\pi_-\sigma$ H ${}^4\Pi$	${}^3P \quad +3K_\pi+ K_\sigma-2J_\pi-J_\sigma$	${}^3P-1.70=-1.70$	
$\pi_+^2\pi_-\sigma$ H ${}^2\Pi$	${}^3P+\frac{3}{2}F_2+3K_\pi+ K_\sigma-\frac{3}{2}J_\pi+J_\sigma$	${}^3P-5.10=-5.10^*$	-5.10

TABLE V. *FH*. ($K=-2.44$, $J_\pi=+1.10$, $J_\sigma=-2.06$.)

STATE	ENERGY EXPRESSION	PREDICTED ENERGY	OBSERVED ENERGY
$\pi_+^2\sigma^2\pi_-$ H ${}^1\Pi$	${}^2P+3K_\pi+2K_\sigma \quad -J_\sigma$	${}^2P-0.33=-0.33$	
$\pi_+^2\sigma^2\pi_-$ H ${}^3\Pi$	${}^2P+3K_\pi+2K_\sigma-2J_\pi-J_\sigma$	${}^2P-2.53=-2.53$	
$\pi_+^2\pi_-^2\sigma$ H ${}^3\Sigma^+$	${}^2P+4K_\pi+ K_\sigma-2J_\pi-J_\sigma$	${}^2P-2.53=-2.53$	
$\pi_+^2\pi_-^2\sigma$ H ${}^1\Sigma^+$	${}^2P+4K_\pi+ K_\sigma-2J_\pi+J_\sigma$	${}^2P-6.65=-6.65^*$	-6.65

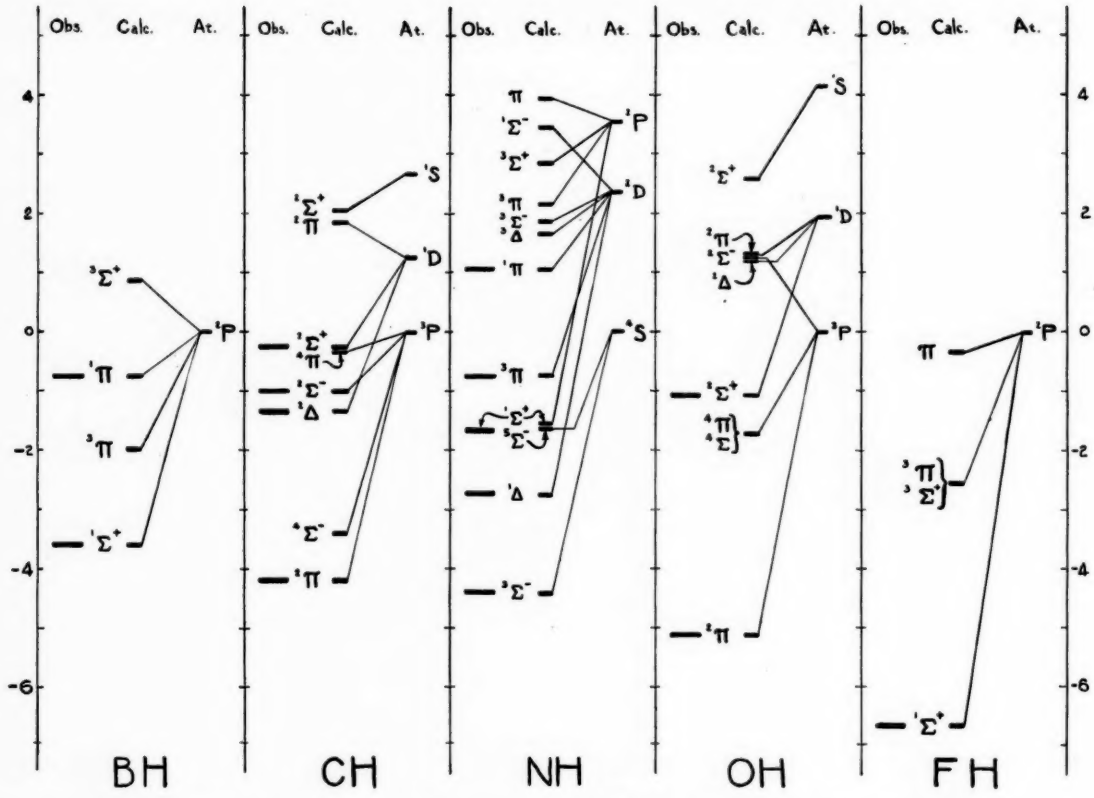


FIG. 2. Energy levels: of molecular states as observed (on the left); of molecular states as calculated here (middle); of the states of the separated atom X (right). Units are electron volts. The origin has been chosen, for each molecule, as the energy of the separated atoms in their normal states. This figure should be compared with Mulliken's Figs. 35–38, reference 16.

RESULTS

(1) The observed energy levels are quite well fitted by the theoretical expressions. This is evident both in the tables and in Fig. 2. It is not entirely due, either, to the obvious fact that we have adjusted parameters to get the best fit. For both CH and NH the theory predicts that a pair of the observed levels should differ by a quantity dependent, not upon the adjustable parameters K, J_π and J_σ, but only upon atomic constants. The evidence, in Table VI, shows this indeed to be the case.

(2) The exchange parameters J_π and J_σ run fairly smoothly from one molecule to the next, as is seen in Fig. 1.

TABLE VI.

MOLECULE	PAIR OF LEVELS	THEORETICAL DIFFERENCE	OBSERVED DIFFERENCE
CH	$^2\Sigma^+ - {}^2\Delta$	$6F_2 = 1.10$ volts	1.08 volts
NH	$^1\Sigma^+ - {}^1\Delta$	$^2P - {}^2D = 1.18$ volts	1.06 volts

The Coulomb parameter K is not so regular. Explicit evaluation of the Coulomb integrals, using simple directive orbitals, would lead one to expect a value for FH on the dashed curve of Fig. 1, about 1–2 volts lower than the value obtained. This is undoubtedly a result of perturbation by an "ionic" configuration.

The $-K$ curve would be even more disrupted if we used the recent lower estimate of the heat of dissociation of OH,[18] for it would have to go 0.5 volt lower at OH than it does. This does not line up at all with expectation, and it is in the wrong direction to be an ionic effect. Therefore the older estimate, 4.9 volts, of the heat of dissociation of OH has been used here and is considered the better one until more conclusive evidence is available.

(3) For levels involving small "promotion" of the H electron (i.e., those which would become low lying levels of the united atom if the H nucleus could be forced gradually into the X nucleus), the predictions here agree well with those made by Mulliken.[20] This can best be seen

[20] Reference 16. The later discovery of the lower $^1\Sigma^+$ state of NH, at a level within 0.3 volt of the estimate of Mulliken's Fig. 37, constitutes striking evidence of the value of his predictions.

by a comparison of Fig. 2 with Mulliken's Figs. 35–38. The unobserved levels which should be stable according to both methods of prediction are the $^3\Pi$ of BH and the $^4\Sigma^-$ of CH. It is very likely that these levels would be observed as stable states if intersystem combinations were not necessary thereto. It is very interesting that this theory confirms Mulliken's predictions for these cases, because the two approaches are basically very different.

(4) For levels involving a large amount of promotion, the predictions made here are much lower than Mulliken's and are probably quite inaccurate. The most striking examples of this are those levels which are quite stable according to this theory but are repulsive by Mulliken's prediction: $^5\Sigma^-$ of NH, $^4\Sigma^-$ and $^4\Pi$ of OH, $^3\Pi$ and $^3\Sigma^-$ of FH. Although these levels, being of higher multiplicity than the observed levels of these molecules, would in any case be difficult to observe, the concept of promotion which is the basis of Mulliken's predictions is too well founded for one to attach much significance to the predictions here. Furthermore, there is considerable evidence that the $^3\Pi$ state of HI is repulsive—further reason for believing that state to be likewise in HF.

Thus it appears that, however lacking in rigor the simplified HLSP theory may be, it does give reasonably accurate predictions of certain levels of the molecules studied here—of the levels, that is, which involve no electron promotion. It is by no means clear why this theory should be even so accurate as it is.[21]

In conclusion, I wish to express my deep gratitude to Professor Van Vleck, whose suggestions were essential to this work, and to thank Professor Mulliken for helpful discussions.

[21] The discussion of Coolidge and James, reference 4, throws much light on the subject, but they admit failure to explain completely the success of "semi-empirical" processes such as the one used here.

MARCH, 1937 JOURNAL OF CHEMICAL PHYSICS VOLUME 5

Energy States of Solids with Particular Reference to the Energy States of $Nd_2(SO_4)_3 \cdot 8H_2O$

F. H. SPEDDING,[1] H. F. HAMLIN AND G. C. NUTTING
The Chemical Laboratories of Cornell University, Ithaca, New York, and the University of California, Berkeley, California

(Received December 11, 1936)

The absorption spectrum of $Nd_2(SO_4)_3 \cdot 8H_2O$ crystals has been photographed at 20°, 78°, 169° and 298°K. The absorption lines occur in multiplets and originate in transitions from two low excited states as well as from the normal state. The excited levels of the basic multiplet are situated 77 and 260 cm^{-1} above the lowest state and undoubtedly arise through splitting of the normal state of the free Nd^{+++} ion in the electric field set up by its immediate neighbors in the crystal lattice. The positions of the observed levels are not in accord with conclusions of Penney and Schlapp from their study of the influence of crystal fields on the temperature variation of the paramagnetic susceptibility of Nd ion in neodymium sulfate octahydrate. Based in part upon the susceptibility measurements of Gorter and de Haas, Penney and Schlapp's work requires that the levels be at 0, 243 and 834 cm^{-1}. If the data of Gorter and de Haas may be considered in error as regards absolute values the positions of the levels we have found are in excellent agreement with predictions of the theories of Van Vleck and Penney and Schlapp, and with the experimental results of Meyer and of Zernicke and James.

VAN VLECK[2] and his associates, using the methods of group theory and wave mechanics, have developed a very attractive theory of the behavior of such energy levels of the common paramagnetic ions as normally contribute to their paramagnetic properties, when the ions are brought into the electric field of their neighboring atoms in a solid. Penney and Schlapp[3] have applied the theory to the specific case of $Nd_2(SO_4)_3 \cdot 8H_2O$. Making the assump-

[1] The major portion of this investigation was carried out under the George Fisher Baker Research Fellowship at Cornell University.

[2] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932).

[3] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

TABLE I. *Frequencies of absorption lines of solid* $Nd_2(SO_4)_3 \cdot 8H_2O$.

20°K			78°K		169°K		298°K			20°K			78°K		169°K		298°K		
Angstroms	Wave Number	Int.	W.N.	Int.	W.N.	Int.	W.N.	Int.	Type	Angstroms	Wave Number	Int.	W.N.	Int.	W.N.	Int.	W.N.	Int.	Type
6838.4	14,619.	3d	14,622.	6wd					h	5104.0	19,587.	5w					18,685.′		
			14,658.	3wd					h	5099.8	19,603.	5w					↓		
6801.9	14,697.	6d	14,700.	6d	14,702.	3d			l	5095.4	19,620.	5w					↓		
6784.9	14,735.	6d	14,737.	6d	14,741.	4wd			l	5085.8	19,657.	3w					↓		
6765.8	14,776.	6d	14,778.	6d	14,780.	4wd				5080.9′	19,676.′		19,678.′				↓		
6747.7	14,816.	5d	14,817.	6d	14,820.	4wd				5068.8	19,723.	4rw	19,702.	7rwd			↓		
			14,873.′		14,875.′					5057.0′	19,769.′		19,727.′		19,753.′		↓		
6713.4	14,891.	4rwd	14,892.	6rwd	14,894.	4rwd				5052.0	19,789.	2d	19,790.	1d			↓		
			14,910.′		14,917.′								19,855.′		19,834.′		continuum		
							15,661.	0rd	h	5046.1	19,812.	1d	19,878.	3rwd	19,875.	2rwd	↓		h
							15,694.	0rd	h				19,902.′		19,917.′		↓		
							15,726.′			5017.5′	19,925.′		19,936.′		19,935.		18,685.′		
							15,762.	0rwd		5012.1	19,946.	4drw	19,948.	3rwd	19,956.	2rwd	↓		l
							15,809.′			5007.1′	19,966.′		19,971.′		19,978.′		↓		
			15,825.	0d					h	4994.0	20,019.	1d	20,024.	0d			↓		
			15,853.	2d	15,853.	0d	15,841.	0rfd	h	4981.7	20,068.	1d	20,069.	0d			20,054.′		
			15,880.	3d	15,881.	0d	15,877.	0rfd	h	4973.8	20,100.	1d							
6287.6	15,900.	6s	15,901.	5s	15,902.	0d			l	4962.9	20,144.	1d	20,138.	0d					
6276.6	15,928.	9s	15,928.	9s	15,928.	6d	15,923.		l	4836.6	20,670.	0d	20,670.	4s					
6265.6	15,956.	9s	15,956.7	9s	15,956.	6d	15,960.		l	4824.9	20,720.	6rs	20,721.	8rs	20,724.	2d	20,713.′		
			15,974.	0d											20,756.′	1rwd	↓		h
			15,985.	0d					h						20,787.′		↓		
6248.9	15,998.	5d	15,998.	6d	15,998.	2rd	15,994.								20,824.′	0rwd	↓		h
6234.4	16,036.	8d	16,036.	9d	16,035.	6d	16,037.								20,875.′		↓		
6224.9	16,060.	7d	16,060.	8d	16,058.	4d	16,059.		s	4774.2	20,940.	3s	20,939.	9d			↓		
			18,055.	1d					h						20,951.	5wd	↓		h
5514.0	18,131.	5d	18,129.	3d	18,131.	0d			l	4770.2	20,957.	3s	20,957.	9d			↓		h
5508.9	18,147.	1d	18,148.	1d						4762.0	20,993.	4s	20,992.	9d			↓		
			18,178.	0rd					h						21,004.	5wd	↓		h
5491.3	18,206.	2d	18,205.	2d	18,205.	0rd				4756.5	21,017.	8rs	21,017.	8s			↓		l
5486.4	18,222.	2d	18,225.	0d						4752.8	21,033.	8rs	21,033.	10s	21,036.	6d	↓		l
5475.1	18,259.	3s	18,259.	2d	18,260.	0d				4744.7	21,069.	8s	21,069.	8s	21,069.	6d	↓		l
5470.1	18,276.	2d	18,276.	0d						4740.0	21,096.	8s	21,091.	8s	21,091.	6wd	↓		l
			18,304	0d					h	4730.7	21,132.	0d					↓		
5454.0	18,330.	2d	18,333.	2d											21,131.′		↓		
5437.5	18,386.	1d	18,385.	1d	18,382.	0d				4727.3	21,148.	6dw	21,146.	8dw	21,147.	5rwd	↓		
5409.7	18,480.	1d	18,480.	1d											21,153.′		↓		
			18,484.	2d						4716.0	21,198.	0d					↓		
5404.4	18,498.	1d	18,498.	2d	18,490.	0d				4714.0	21,207.	0d					↓		
5389.6	18,549.	0d	18,553.	1d	18,546.	0d				4711.9	21,217.	7d	21,218.	8d	21,215.	5d	↓		
5373.3	18,605	0d	18,610.	0d	18,614.	0d				4707.8	21,235.	7rs	21,235.	4rs			↓		
			18,720.	0d	18,721.	2d				4705.9	21,243.	0rd					↓		
			18,760.	2rd	18,761.	3rd	18,685.′		h		21,276.′		21,274.′		21,269.′		continuum		
					18,786.′					4695.9	21,289.	6rwd	21,289.	7rwd	21,287.	6rwd	↓		
			18,805.	2rd	18,801.	4rwd			h		21,303.′		21,304.′		21,306.′		↓		
					18,818.′					4689.7	21,317.	0rd					↓		
					18,830.′					4684.9	21,338.	0rd					↓		
			18,845.	0rd	18,856	2rwd				4681.0	21,356.	0rd					↓		
					18,884.′					4673.3	21,392.	6rd	21,394.	7rd	21,395.	6rd	↓		
			18,907.	0s	18,900.	1d			h	4663.8	21,430	0d	21,435.	1d			↓		
					18,925.′					4659.9	21,453.	2d					↓		
5277.3	18,944.	6s	18,946.	10d	18,947.	3rwd			h	4657.7	21,463.	8s	21,463.	8s	21,464.	4d	↓		
					18,961.′					4647.3	21,511.	6d	21,513.	3d	21,518.	2rd	↓		
					18,980.′					4638.8	21,551.	4rd	21,550.	3rd			↓		
5262.9	18,996.	6rs	18,996.	10rd	18,997.	2rwd			h		21,568.′		21,570.′				↓		
					19,014.′					4631.9	21,583.	3rwd	21,581.	2rwd			↓		
					19,020.′						21,597.′		21,593.′				↓		
5255.9	19,021.	8rs	19,025.	10rd	19,030.	2rd				4625 5	21,613.	4dw	21,615.	3dw			↓		
					19,040.′					4618.3	21,647.	2rd	too diffuse		21,643.	0rwd	↓		
5243.7′	19,065.′		19,057.′		19,052.′					4605.9	21,705.	2dw	21,705.	2dw			↓		
5242.1	19,070.	7rwd	19,085.	10	19,082.	2rwd				4586.9	21,795.	4dw					↓		
5237.8′	19,087.′		19,113.′	rwd	19,123.′								21,799.	3dw	21,800.	3dw	↓		
5228.8	19,120.	2s								4584.8	21,805.	2d					↓		
5226.9	19,127.	1s											21,906.′		21,896.′		↓		
5224.2	19,136.	1s								4559.3	21,927.	4rwd	21,931.	7rwd	21,927.	2rwd	↓		
5223.3′	19,139.′		19,142.′		19,140.′								21,957.′		21,959.′		↓		
5215.3	19,169.	6rwd	19,168.	9rwd	19,181.	2rwd				4470.9	22,361.	0d					21,935.′		
5207.7′	19,197.′		19,195.′		19,224.′					4460.3	22,414.	2rd							
5206.3	19,202.	2d								4456.0	22,435.	2d							
5203.7	19,212.	2d								4447.7	22,477.	0rd							
5200.9	19,222.	2d								4446.6	22,483.	0d							
5198.8	19,230.	1d								4431.0	22,562.	1rd							
5195.2	19,243.	2d								4424.3	22,596.	0d							
5187.7	19,271.	2d								4411.1	22,664.	0d							
5185.8	19,278.	3d															23,014.	2d	h
5177.6	19,309.	1d											23,045.	0d	23,043.	0d	23,035.′		
					19,265.′												23,071.	6rwd	h
5174.6	19,320	1d			19,327.	2rwd							23,080.	4d	23,079.	4d	23,109.′		
5164.4	19,358	1d	19,369.	7d	19,391.′				h								23,221.′		
5159.6	19,376.	0d								4303.5	23,230.	3s	23,229.	9s	23,229.	6s	23,233.	4d	h
5156.0	19,390	1d															23,246.′		
5150.0	19,412.	1d															23,290.′		
5142.9	19,439.	6d	19,443.	8d	19,435.′					4289.3	23,306.	9ws	23,305.	10ws	23,304.	8sw	23,310.	8rwd	l
5139.9	19,450.	8d			↓												23,331.′		
5135.2	19,468.	0d								4286.5	23,332.	2s							
5132.9	19,477.	0d	19,475.	7wd						4281.7	23,348.	4d	23,346.	2d					l
5120.7	19,523.	6wd	19,500.′							4279.8	23,359.	3s	23,356.	5s					
			19,534.	8rwd		2rwd				4278.8	23,364.	3s	23,368.	3s					
5112 8	19,553.	6wd	19,567.′		↓		↓			4277.7	23,371.	4s							

tions that the field about the Nd ion has cubic symmetry and that there is L–S coupling in the ion's lowest state, they are able to account for the magnetic susceptibility data of Gorter and de Haas[4] over the temperature range 14° to 300°K. It is to be regretted that there are not more cryogenic susceptibility measurements for neodymium sulfate, especially since the magneton number given by Gorter and de Haas for 300° is notably different from the values found earlier by Meyer[5] and by Zernicke and James.[6]

While the theory is in excellent agreement with Gorter and de Haas' work on Nd it is not completely satisfactory for these reasons. (1) Crystallographically and chemically the octahydrated sulfates of the rare earths (always excepting Ce) are very closely similar and there can be little doubt that the lattice structures of all are the same. It follows that for all the rare earths the strength of the crystal field acting on a rare earth ion in its dependence upon direction and distance from the ion must be nearly the same. Especially is this true of adjacent elements. Penney and Schlapp have found, though, that in order to duplicate the susceptibility-temperature curves of Gorter and de Haas for $Nd_2(SO_4)_3 \cdot 8H_2O$ and $Pr_2(SO_4)_3 \cdot 8H_2O$ it is necessary to assume that there is about the metal ions a potential field whose constant D[7] for Nd is about four times as large as that for Pr. (2) According to Gorter and de Haas' data for $Nd_2(SO_4)_3 \cdot 8H_2O$, Nd^{+++}, whose normal state is $4f^3\ {}^4I_{9/2}$, has a magnetic susceptibility which at low temperatures deviates sharply from the values calculated for the free (gaseous) ion, and which approaches the gas values only at relatively high temperatures. Er, complementary element of Nd in the second half of the rare

[4] C. J. Gorter and W. J. de Haas, Leiden Commun. 218 *b*.
[5] S. Meyer, Physik Zeits. **26**, 51, 478 (1925).
[6] J. Zernicke and C. James, J. Am. Chem. Soc. **48**, 2827 (1926).

[7] Penney and Schlapp write for the potential energy of an electron of a Pr or Nd ion in the electric field of the atoms which envelop it the expression $V=D(x^4+y^4+z^4)$. The field has cubic symmetry and the origin of coordinates is taken as the center of the rare earth ion.

TABLE I.—*Continued.*

20°K			78°K		169°K		298°K			20°K			78°K		169°K		298°K		
Angstroms	Wave Number	Int.	W.N.	Int.	W.N.	Int.	W.N.	Int.	Type	Angstroms	Wave Number	Int.	W.N.	Int.	W.N.	Int.	W.N.	Int.	Type
4269.2	23,417.	0*wd*								4000.6	24,989.	5*s*	24,990.	0*d*					
4264.4	23,444.	0*wd*											26,101.	5*s*	26,101.	3*d*	26,114.	1*d*	*h*
4257.4	23,482.	0*wd*								3818.9	26,178.	10*vs*	26,178.	9*s*	26,178.	7*s*	26,184.	3*d*	*l*
4244.7	23,552.	0*d*								3804.7	26,276.	10*s*	26,274.	5*s*	26,272.	3*d*	26,272.	1*d*	
4238.0	23,590.	0*d*																	
4234.4	23,609.	0*d*								3751.6	26,648.	6*vs*	26,648.	2*s*	26,654.	1*d*			
4228.3	23,644.	5*s*	23,645.	2*s*						3747.4	26,678.	3*s*	26,676.	4*s*					
4223.5	23,670.	4*d*	23,672.	0*d*															
			23,684.	4*d*	23,685.	0*d*			*h*	3741.7	26,718.	9*vs*	26,717.	4*s*	26,720.	2*d*	26,731.	0*d*	
4211.4	23,738.	3*d*	23,735.	0*d*						3739.7	26,732.	1*s*							
4207.3	23,762.	10*vs*	23,761.	10*s*	23,759.	6*d*	23,765.	3*d*	*l*	3736.8	26,753.	0*s*							
			23,806.	0*d*	23,812.	0*d*			*h*										
4186.8	23,878.	5*d*	23,883.	0*d*	23,885.	0*d*			*l*	3624.4	27,583.	1*d*	27,587.	1*d*	27,589.	0*d*			
4181.6	23,908.	1*d*								3621 9	27,602.	0*d*							
4177.5	23,931.	3*s*								3619.3	27.622.	3*s*	27,623.	2*d*					
4175.5	23,943.	7*sw*	23,947.	1*d*	23,946.	1*d*				3614.9	27,655.	5*s*	27,655.	4*d*	27,659.	0*d*			
4173.2	23,956.	8*s*	23,954	0*d*	"					3604.8	27,733.	1*d*	27,737.	1*d*	27,738.	3*d*			
4169.2	23,979.	2*d*											27,782.	2*d*	27,783.	3*d*			*h*
4163.5	24,012.	1*d*											27,817.	3*d*	27,815.	5*d*			*h*
4153.0	24,072.	4*s*	24,073.	0*d*									27,944.′						
4145.3	24,117.	6*d*	24,121.	0*d*	24,126.	0*d*				3574.3	27,969.	10*vs*	27,973.	8*vwd*					
4070.3	24,562.	8*vs*	24,562.	3*s*	24,564.	0*d*	24,572.	0*d*					27,992.′						
4056.9	24 642.	1*s*											28,019.′						
4054.7	24,656.	1*s*								3564.7	28,045.	10*sw*	28,044.	8*vwd*					*l*
4050.8	24,680.	0*s*											28,069.′						
							24,772.	0*d*					29,019.	4*s*	29,024.	3*s*			
4020.5	24,865.	10*s*	24,866.	7*s*	24,862.	3*d*	24,879.	2*d*					29,039.	0*s*					
4010.2	24,929.	4*s*	24,932.	0*d*						3438.4	29,075.	3*s*	29,074.	1*s*					
4007.9	24,944.	9*vs*	24,944.	2*s*	24,947.	1*d*				3435.7	29,098.	10*vs*	29,099.	6*s*	29,099.	5*wd*			
4006.2	24,954.	7*s*	24,954.	1*s*									29,326.	2*d*					
4003.8	24,969.	7*s*	24,971.	1*d*	24,968.	1*d*	24,965.	0*d*					29,348.	0*d*					
4002.3	24,979.	3*s*				"				3401.5	29,391.	0*dw*	29,401.	3*d*	29,405.	0*d*			

w=15–30 cm^{-1} width.
vw=more than 30 cm^{-1} width.
vs=very sharp, very well defined line.
s=sharp, well defined line.
d=diffuse, poorly defined.
vd=very diffuse, very poorly defined line.
h=high temperature line (see text).
l=low temperature line (see text).

The intensities given are visual approximations made by the author for each plate on a scale of 0–10. 0 intensity was too faint to be seen under the comparator, and the plate had to be scratched to measure. 1 intensity was very faint and was also scratched, 2–5 intensity were rather faint, and 5–10 strong absorption, 10 being complete in the center of the line or band. The probable errors of the lines designated as sharp are: 0 and 1 intensity about 5 cm^{-1}, 2 and 3 about 3 cm^{-1}, 4–6 about 1 cm^{-1}, 6–10 about 0.5 cm^{-1}. The probable error of the diffuse lines are: (0 and 1) intensity about 10 cm^{-1}, 2–5 about 5 cm^{-1}, 6 and 7 about 3 cm^{-1}, 8–10 about 2 cm^{-1}. This error will of course depend on the position of the lines on the plate.

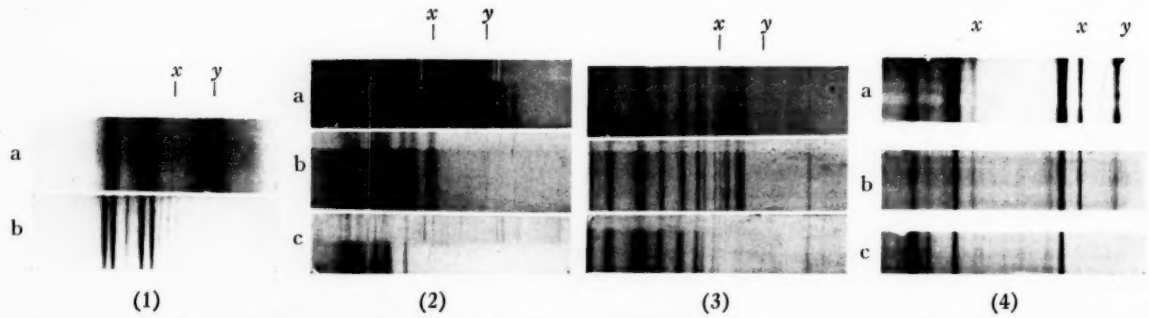


FIG. 1. (1) Multiplet at 16,000 cm^{-1}. Prism spectrograph a, 300°K, b, 78°K. (2) Multiplet at 19,000 cm^{-1}. Grating spectrograph. (3) Multiplet at 21,000 cm^{-1}. Grating spectrograph. (4) Multiplet at 23,300 cm^{-1}. Grating spectrograph. a, 169°K, b, 78°K, c, 20°K. *x*, lines originating at the 77 cm^{-1} level. *y*, lines originating at the 260 cm^{-1} level.

earth group, also has a ^4I normal state in its salts. Susceptibility measurements of $Er_2(SO_4)_3 \cdot 8H_2O$ by de Haas, Wiersma and Capel[8] indicate almost perfectly gas-like behavior for Er^{+++} over the entire temperature range 14°–285°K.[9] In view of the similarity of the two elements, if the theory is made to agree with the data for Nd it is not to be expected that it will agree with that for Er.[10] (3) Although the normal state of Sm^{+++}, $^6H_{5/2}$, may split into only two states in a cubic field (into three in a field of lower symmetry) at least four low levels besides the normal one have been found spectroscopically.[11] (4) In the theory of the susceptibility of Nd^{+++} a crystal field of predominantly cubic symmetry is assumed and the attempt to substitute for it a predominantly rhombic field has been definitely unsuccessful. Since the crystallographic symmetry is monoclinic it might be expected that there would be less than cubic symmetry about the Nd ion. From this it follows that the field about the rare earth ion is determined almost entirely by its envelope of oxygen atoms situated, presumably, at the corners of an octahedron not appreciably distorted by the sulfate ions (which very likely furnish some of the oxygen atoms since enough of them are not provided by water molecules alone).

In view of the shortcomings of the susceptibility theory a spectroscopic investigation of the energy states of $Nd_2(SO_4)_3 \cdot 8H_2O$ is of particular interest.

EXPERIMENTAL PART

The work was begun at the University of California where one set of plates of the absorption spectrum of neodymium sulfate was obtained at each of the following temperatures, 20°K, 78°K, 169°K, 300°K. A complete description of the apparatus and procedure has been given already.[12] The salt was used in the form of conglomerates of small crystals and the thickness was from 3 to 5 mm. The origin of the neodymium is unknown but its purity is adequate for the only foreign substance present in detectable amount is Pr, whose strongest absorption lines show faintly in the spectra of thick conglomerates.

A second series of spectra was photographed at the temperatures 78° and 300°K with the large glass single prism spectrograph of the chemistry department of Cornell University. The dispersion is such that the visible spectrum is spread over about 20 cm. The procedure was exactly the same as at California. The neodymium used was some which Dr. H. N. McCoy very generously presented to one of us to further research along these lines. It is of somewhat better purity than that used at California. All the plates were measured on the large comparator belonging to the Cornell physics department.

[8] W. J. de Haas, E. C. Wiersma and W. H. Capel, Leiden Commun. 201 *b*.

[9] Something seems to be wrong with at least the absolute values of the susceptibility of $Er_2(SO_4)_3 \cdot 8H_2O$, for the magneton number of 44.8 at room temperature reported by de Haas, Wiersma and Capel is very much smaller than the most probable one, 47.3, given by Gorter (Dissertation, Leiden, 1932). A repetition of the Er measurements has been promised.

[10] Spedding, Phys. Rev. **50**, 574 (1936).

[11] F. H. Spedding and R. S. Bear, Phys. Rev. **46**, 975 (1934).

[12] F. H. Spedding and R. S. Bear, Phys. Rev. **42**, 58 (1932); F. H. Spedding and G. C. Nutting, J. Chem. Phys. **2**, 422 (1934).

The accuracy of measurement, of course, varies greatly since it depends upon the sharpness of the lines and their intensity, the temperature at which the spectra were photographed, and the region of the plate. We think that in general the positions reported for the sharpest lines in the most favorable region of the plate are correct within 0.2 cm^{-1}, while in the case of the weak, diffuse bands the error may be as much as 20 cm^{-1}. For most lines the error is probably not more than 2 cm^{-1}. Many of the lines and bands are so faint that they are invisible under the magnification of the measuring engine, hence their positions were marked by fine scratches in the gelatine made by a needle with the aid of a low power eyepiece.

Data giving the position, intensity and character of the lines is presented in Table I. From these data a rough estimate of the accuracy of individual measurements may also be obtained. The intensities have been gauged visually on the scale 0–10 and are principally useful in estimating relative intensities of adjacent lines. Even here they are valid only for a conglomerate of given thickness and particle size because[13] in a photograph of the absorption spectrum of a conglomerate the frequencies weakly absorbed appear relatively more prominently than the ones strongly absorbed.

The existence of excited levels lying close to the basic state has been determined by two independent methods. The first takes advantage of the fact that the intensity of absorption is proportional to the number of absorbers in the lower state. This in turn is determined by the absolute temperature according to the Boltzmann relation. All lines originating at a given excited state must fade out with more or less suddenness as the temperature is lowered beyond a certain point, and from this temperature one can calculate roughly the separation of the normal and the excited states. Fig. 1 shows several examples of this phenomenon.

The second method depends upon the fact that if absorption lines arising from two lower levels and terminating in a variety of common upper levels occur in the spectrum, a constant frequency interval equal to the separation between the lower levels is found repeatedly throughout the spectrum. An excited lower level of neodymium sulfate 77 cm^{-1} above the normal one has been discovered in this way and the best evidence for it is listed in Table II.

By means of the first method it is established beyond doubt that at least one level must exist between 250 and 300 cm^{-1} (see Fig. 1). It is unfortunate that transitions beginning at this excited level are infrequent until the temperature of the crystal is rather high. The corresponding absorption lines are then usually so wide and so diffuse that their positions cannot be measured with high accuracy. A further complication is introduced by the fact that the levels comprising the multiplets of the upper state most often are so close together that at the temperatures in question thermal broadening as a rule causes the absorption lines to fuse. This makes it very

TABLE II. *77 cm^{-1} levels.*

78°K		
l	h	$\Delta\nu$
14,737.	−14,658.	79.
14,700.	−14,622.	78.
15,901.	−15,825.	76.
15,928.	−15,853.	75.
15,956.7	−15,880.	76.7
16,060.	−15,985.	75.
18,129.	−18,054.	75.
18,259.	−18,178.	81.
18,384.	−18,304.	80.
19,025.	−18,946.	77.
19,071.	−18,996.	75.
19,443.	−19,368.	75.
19,955.	−19,879.	76.
21,017.	−20,939.	78.
21,033.	−20,957.	76.
21,069.	−20,992.	77.
23,305.	−23,229.	76.
23,761.	−23,684.	77.
23,883.	−23,806.	77.
26,178.	−26,101.	77.

TABLE III. *260 cm^{-1} levels.*

78°K		$\Delta\nu$
15,661 (*RT*)	−15,923 (*RT*)	262
15,694 (*RT*)	−15,960 (*RT*)	266
18,760	−19,025	265
18,805	−19,070 (*h*)	265
18,907	−19,168	261
20,787 (*e*)	−21,033	*s* 260
20,756	−21,017	
20,824	−21,091	*s* 260
20,875		
23,045	−23,305	260
23,080	−23,346	266
27,782	−28,044	262

s =about, h =20°K, e =169°K, RT =300°K.

[13] F. H. Spedding and R. S. Bear, Phys. Rev. **39**, 948 (1932).

unusual to find clear cases of constant energy differences. There are, however, a few such cases in which $\Delta\nu$ is about 260 cm^{-1} and this separation accounts for all the instances discovered solely by Method I within our limits of error of estimation (Table III).

The spectra resemble in a general way those reported earlier for Sm.[12] The absorption lines are grouped in multiplets which are scattered through the visible and near ultraviolet. In the case of Nd there are fewer multiplets than were found for Sm, and these usually have more lines.

14,700 cm^{-1} multiplet

This prominent group is typical of a number of such groups to the extent that its lines are diffuse and wide even at 20°. The lines are almost certainly complex and have not been resolved due either to lack of a sufficiently low temperature or more probably due to a broadening of the levels brought about by the neighboring atoms in the solid. Lines arising from the 77 cm^{-1} level appear associated with the two intense long wave-length lines of the multiplet. Whether or not high temperature lines[14] are associated with other intense low temperature lines cannot be determined from our data since the low temperature lines are so spaced that they lie where the high temperature lines are expected to occur, thus masking them if they do exist. It is true in general that high temperature lines can be distinguished clearly only at the long wave-length edge of a multiplet, for the upper levels are usually so close together that high temperature lines in the body of a multiplet fall on or near the long wave-length components of the multiplet arising from the normal state.

15,900 cm^{-1} multiplet

The lines of this multiplet are unusually intense. Several of them originate at levels 250 cm^{-1} or more above the normal one and in the case of two pairs of lines measurable with somewhat greater precision than the rest the separation is close to 260 cm^{-1}. In this as in most of the multiplets there is positive evidence for the existence of the 77 cm^{-1} level.

17,500 cm^{-1} multiplet

General absorption apparently underlies the discrete structure making accurate measurements impossible. Many lines present are not being reported because of their excessive faintness, diffuseness and lack of resolution. Likewise evidence for the 77 cm^{-1} and 260 cm^{-1} levels is being withheld because of its too great degree of uncertainty. A second unfortunate circumstance is that the junction of the grating plates has usually chanced to occur within this multiplet.

18,250 cm^{-1} multiplet

The absorption in this multiplet also is extremely weak and therefore very difficult to measure. At 169° and above it is scarcely visible.

19,000–19,600 multiplets

These are two of the most intense multiplets in the spectrum. The strong components, most of which are diffuse, overlay a background of fainter lines that sometimes are so little separated from their strong companions as to make correct measurement of the position of the latter doubly difficult. Here again there is a considerable amount of evidence for excited levels at 77 and 260 cm^{-1}.

In the region between *17,500 and 23,000 cm^{-1}* there is an almost continuous succession of very faint lines which in the main are probably attributable to Nd but which in some cases may be due to impurities. Superimposed upon this background are the intense multiplets which we have measured. At frequencies higher than 23,000 cm^{-1} are a number of groups of well-defined lines which further substantiate our assertion that there is a level at 77 cm^{-1}.

Discussion of Results

Hund[15] predicted the character of the normal states of the rare earth ions in solid salts, assuming the validity of the usual coupling rules for gaseous atoms. He then computed the magnetic susceptibilities of the ions, supposing that only the normal states contribute appreciably toward their paramagnetic properties. Agreement with the experimental values for temperatures of 300°K and higher is good for all the rare earths except Sm and Eu. Frank[16] has shown that very important corrections, due to the contribution of the other levels of the normal multiplet and especially due to interaction among the lowest levels, must be added to the Hund values for Sm and Eu. Corresponding corrections for Nd amount to only about three percent, and for our purpose may be neglected.

In Hund's work it is implicit that the interaction energy of J with the crystal field is always small compared with kT, and while the assumption is clearly justified by experiment at room temperature and above, it is expected and is often found to be invalid at low temperatures. Penney and Schlapp have been able to predict

[14] By low temperature lines we mean those originating at the normal state and by high temperature lines those originating at the excited lower states.

[15] F. Hund, Zeits. f. Physik **33**, 855 (1925).

[16] A. Frank, Phys. Rev. **39**, 119 (1932).

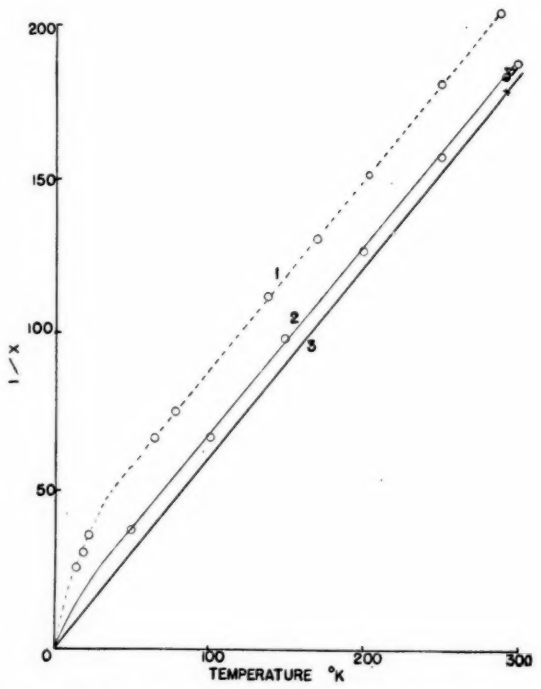


FIG. 2. (1) o Gorter and de Haas' experimental points. --- Penney and Schlapp's theoretical curve. (2) -o-o Penney and Schlapp's theoretical curve using our levels. (3) Hund's curve. oΔ, Meyer and Zernicke and James experimental points. X, Cabrera's experimental point.

the relative position of the three levels of Nd^{+++} produced by splitting of its normal state in a crystal field of cubic symmetry, and of the ten levels which result from superposition of a magnetic field upon the crystal field. In order to determine the actual $\Delta\nu$'s recourse to experiment must be had, and from extrapolation of measurements of Gorter and de Haas, Penney and Schlapp have determined the over-all separation of the multiplet in the absence of a magnetic field to be 834 cm^{-1}. It then follows from their own work that the intermediate level is 243 cm^{-1} above the lowest one. As has been said earlier the calculated variation of susceptibility with temperature for $Nd_2(SO_4)_3 \cdot 8H_2O$ agrees very closely with that measured.

Our findings are in definite disaccord with these predictions. In addition, using our spectroscopically determined levels, we are not able to reproduce the experimental temperature-susceptibility curve by any known relationship between susceptibility and energy states. If we may assume that the susceptibility measurements of Gorter and de Haas are in some measure incorrect and that the multiplet interval 834 cm^{-1} deduced from those measurements is likewise incorrect, we discover that our results are in excellent agreement with Penney and Schlapp's conclusions. The relative positions of the multiplet levels which they suggest and which are expressed by the numbers 0, 243 and 834 are virtually identical with those we have found at 0, 77 cm^{-1} and 260 cm^{-1}. The assertion (based on the data of Gorter and de Haas) that the crystal field has predominantly cubic rather than predominantly rhombic symmetry is likewise substantiated. Splitting of the "cubic" levels by a field of rhombic symmetry would have an inappreciable effect on the susceptibility so long as the amount of the splitting is small compared with that produced by the cubic field, but it should be easily detected spectroscopically. In Fig. 2 are presented plots of magnetic susceptibility *vs.* temperature for $Nd_2(SO_4)_3 \cdot 8H_2O$ as calculated by Hund, as measured by Gorter and de Haas, and as calculated by means of the equation of Penney and Schlapp, using our data. This last plot has less curvature than that of Gorter and de Haas and more closely resembles that for the free gaseous ion given by Hund. It is, furthermore, in agreement with the experimental values of the susceptibility at room temperature found by Meyer and Zernicke and James.[17] The curve is more nearly of the type of that for erbium, so that one objection mentioned in the introduction is thus removed.[10] This phase of the problem will be discussed in detail in a later paper on erbium. Finally, the field constant D is only one-third as large as that calculated by

[17] The experimental work in this field is not at all satisfactory as the various investigators do not agree among themselves. Thus Selwood, J. Am. Chem. Soc. **55**, 3161 (1933), gives the following summary of values at room temperature for $Nd_2(SO_4)_3 \cdot 8H_2O$:

	Specific Susceptibility $\times 10^6$
Wedekind	14.5
S. Meyer	14.6
Cabrera	15.4
Zernicke and James	14.5
Gorter and de Haas	13.08
Selwood	14.6

Selwood's results at liquid-air temperature, however, do not agree with our calculated ones nor do they agree with the experimental ones of Gorter and de Haas. Recently Jackson, Proc. Phys. Soc. (Sept. 1936), stated his results check Gorter and de Haas' within the experimental error but is not very specific as to the magnitude of his errors.

Penney and Schlapp[18] and has almost the same value as the constant they give for Pr (which, incidentally, may not be quite right for the magneton number of $Pr_2(SO_4)_3 \cdot 8H_2O$ determined by Gorter and de Haas is appreciably different from those reported by other investigators).

The anomaly of samarium, which was referred to in the introduction, remains, supporting Spedding's contention that there must be in Sm^{+++} an extra electronic level which lies near the normal state. There is no doubling of the levels of Nd^{+++} as in the case of Sm^{+++} and thus the view of Van Vleck and Frank that the supernumerary levels are of vibrational origin seems unlikely to be correct. Owing to the close similarity of corresponding salts of different rare earths it does not appear probable that a vibrational level should occur in Sm and not in Nd or Gd, elements on either side of it in the periodic table.

Just as in the instance of Sm a measurement of the heat capacity of $Nd_2(SO_4)_3 \cdot 8H_2O$ in the range 14°–300°K would be of interest. Chemically and crystallographically the rare earth sulfate octahydrates are so nearly alike that their vibrational and lattice frequencies should be the same except for mass corrections. Considering the pair of salts $Nd_2(SO_4)_3 \cdot 8H_2O$ and $Gd_2(SO_4)_3 \cdot 8H_2O$, since the molecular weights differ by less than 4 percent the mass correction should be very small. Any difference in the heat capacity of the salts should then be due to differences in their electronic states. The normal state of Gd^{+++} is single so that the curve of the heat capacity difference between the Gd and Nd salts plotted against absolute temperature should show humps at the temperatures at which the 77 and 260 cm^{-1} levels of Nd^{+++} become appreciably populated.

We wish to thank Dr. H. N. McCoy for his generous gift of the neodymium, and Professor R. C. Gibbs of the Cornell University Physics Department for the use of the measuring engine.

[18] Professor Van Vleck writes us the following comments regarding the determination of the field-constant D from the experimental data of Gorter and de Haas on $ND_2(SO_4)_3 \cdot 8H_2O$. "As suggested by Dr. Gorter, the value of D is much less sensitive to errors in calibration if based exclusively on the measurements at very low temperatures rather than primarily on the absolute susceptibility at room temperatures as in the original paper of Penney and Schlapp. When T is sufficiently low, the susceptibility should theoretically obey a formula of the form $X = AT^{-1} + B$, and such an expression is approximately satisfied by the Leiden data below 20°K. As Gorter points out, a determination of D entirely independent of calibration is obtained from the experimental value of B/A if one assumes that A has the theoretical value corresponding to $1.83(8/11) \cdot \sqrt{3} = 2.3$ Bohr magnetons. By this method, a value of D is found which is 6 percent lower than that found by Penney and Schlapp for $Pr_2(SO_4)_3 \cdot 8H_2O$. At first sight it thus appears that the glaring discrepancy between Pr and Nd by a factor 3.9 as reported by Penney and Schlapp is removed, but unfortunately the experimental value of A does not check with theory, and yields a magneton number only 1.7. It is entirely inconceivable that the calibration error is as great as a factor $(2.3/1.7)^2$, and if A corresponds to a magneton number only 1.7, the value of D for $Nd_2(SO_4)_3 \cdot 8H_2O$ is 80 percent greater than for $Pr_2(SO_4)_3 \cdot 8H_2O$. Much more serious than this discrepancy, however, is the fact that the experimental data on A yield a magneton number so much lower than the minimum possible value 2.3 for a cubic field. This difficulty was not mentioned in the Penney and Schlapp article, and casts doubt on either the adequacy of the simple crystalline potential model or else on the cubic character of the crystalline field."

The Thermal Decomposition of Ethane

Remarks About a Paper by E. W. R. Steacie and N. W. F. Phillips

(J. Chem. Phys. **4**, 461 (1936))

HANS SACHSSE
Ludwigshafen am Rhein, Germany

(Received November 10, 1936)

On account of the experimental value of the reaction $D+C_2H_6$ according to Steacie and Phillips the radical chain mechanism in the decomposition of ethane by F. O. Rice is anew discussed. It results that even now this theory does not agree with the experiment.

THE radical chain theory of the thermal decomposition advanced by F. O. Rice[1] was tested by Patat and Sachsse[2] by measuring the radical concentration during decomposition. Especially in the case of ethane Sachsse[3] found a H atom concentration three powers of ten smaller than that required by the calculation of Rice and Herzfeld.

Recently Steacie and Phillips[4] have studied the reaction of D atoms produced by an electrical discharge with ethane according to the equation: $D+C_2H_6=HD+C_2H_5$. They found for this reaction at room temperature a heat of activation of 6300 cal. with a steric factor of 0.1. For the reaction of H atoms with ethane they assume a value of equal magnitude. With this value they revise the calculation of Rice and Herzfeld who had used 17,000 cal. for the said reaction. They conclude that on the account of the new value the H atom concentration required by the chain mechanism is now considerably smaller, and they say that it agrees almost exactly with our experimental value. The first part of this sentence is doubtless right, but the conclusion of the exact conformity is based on a misunderstanding.[5]

Therefore using the new value of Steacie and Phillips in the following we shall calculate once more as accurately as possible the radical concentration required by the chain mechanism, while discussing various assumptions, and shall compare the result with experiment. For such an exact numerical comparison ethane appears to be the most adequate example. For firstly, its chain mechanism is especially obvious and simple, and in the second place the chain carrier itself, the H atom, can be determined directly by the parahydrogen method; thus the number of required assumptions is less here than in other decomposition processes.

According to the assumptions of Rice and Herzfeld the decomposition of ethane proceeds by the following steps:

$$C_2H_6 \rightarrow 2CH_3, \qquad C_1 e^{-E_1/RT}, \qquad (1)$$

$$CH_3+C_2H_6 \rightarrow C_2H_5+CH_4, \qquad a_2Z_2e^{-E_2/RT}, \qquad (2)$$

$$C_2H_5 \rightarrow C_2H_4+H, \qquad C_3e^{-E_3/RT}, \qquad (3)$$

$$H+C_2H_6 \rightarrow C_2H_5+H_2, \qquad a_4Z_4e^{-E_4/RT}, \qquad (4)$$

$$H+H \rightarrow H_2, \qquad (5)$$

$$H+C_2H_5 \rightarrow H_2+C_2H_4, \qquad a_6Z_6e^{-E_6/RT}. \qquad (6a)$$

$$H+C_2H_5 \rightarrow C_2H_6. \qquad (6b)$$

Here C signifies the constants of the monomolecular decomposition processes which are independent of temperature, Z the collision numbers, and a the corresponding steric factors. For the stationary radical concentrations the authors arrive at:

$$[H]=(k_1k_3/2K_4K_6)^{\frac{1}{2}}, \quad [CH_3]=K_1/K_3,$$
$$[C_2H_5]=[C_2H_6]\cdot(K_1K_4/2k_6k_3)^{\frac{1}{2}}.$$

In the Table I the H atom concentration and the velocity constant are calculated and com-

[1] F. O. Rice, J. Am. Chem. Soc. **53** (1931); F. O. Rice, K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).
[2] F. Patat, H. Sachsse, Nachr. Ges. Wiss. Goettingen **1**, 41 (1934); Zeits. f. physik. Chemie **B31**, 105 (1935).
[3] H. Sachsse, Zeits. f. physik. Chemie **B31**, 79 (1935).
[4] Steacie and Phillips, J. Chem. Phys. **4**, 461 (1936).
[5] In their calculation the authors apparently use the figures of my Table 3, Zeits. f. physik. Chemie **31**, 85 (1935). But these figures have not been calculated on the basis of the Rice-Herzfeld mechanism. They only are to be used with a mechanism meeting the following condition: $H=\text{const.}\ 1/k_4$. This is not the case with the mechanism of F. O. Rice and it would be difficult to suggest such a mechanism for the decomposition of ethane which at the same time gives the correct order for the decomposition.

TABLE I. *H atom concentration and velocity of reaction calculated according to the radical chain theory supposing different values of the fractional reactions.*

C_1	E_1	C_3	E_3	a_4	E_4	a_6	E_6	$[H]\cdot10^{12}$ calc.	log k calc.
10^{14}	80	10^{14}	49	0.1	6.3	0.1	8	320	$14\ -63500/2.3RT$
10^{14}	80	10^{14}	49	0.1	6.3	10^{-3}*	0	310	$15\ -67500/2.3RT$
10^{14}	71	10^{14}	49	0.1	6.3	0.1	8	4350	$14\ -58500/2.3RT$
$10^{13.5}$	80	$10^{13.5}$	49	0.1	6.3	0.1	8	103	$13.5-63500/2.3RT$
								$[H]\cdot10^{12}$ observed	log k observed
								6.3	$14.5-69800/2.3RT$

* Ternary collision.

pared with the experimental values using different data for the several partial reactions. For the collision diameter of C_2H_6 and C_2H_5 there has been used 3.3A, for that of H 2.3A. The main uncertainty is caused by the constants C_1 and C_3 for which Rice and Herzfeld give the value 10^{14}. Taking this uncertainty into account in one calculation there has been inserted $10^{13.5}$ for these two constants to give a more favorable chance for the chain mechanism. In the assumptions of Rice the values of E_1 and E_3 are already relatively high, though in fact they are rather lower than higher. Particularly for the dissociation energy of ethane besides the value of Rice there is also to be considered the lower value of 71,000 cal. resulting from the general strength of the C—C linking. In consequence of the determination of Steacie and Phillips there would probably be not much change of a_4 and E_4, also a_6 and E_6 hardly cause uncertainty, this reaction *per se* already being supposed to be rapid. As may be noted, it remains the same whether one supposes a triple collision or a rapid bimolecular reaction causing the chain rupture.

As may be noted, there is still a substantial discrepancy between experiment and theory even if all suppositions for the chain mechanism are as favorable as possible. Also the activation energies show a discrepancy far beyond the limits of error compared with my determination of 69,800 cal. or with that of Mareck and McCluer[6] of 73,000 cal. Smaller values of C_1 and C_3 give no agreement at all with the experimental C-factor of 14.5 (H.S.) or 15.2 (Mareck and McCluer).

Finally we have still to discuss whether the decomposition is caused by chain reactions even if one rejects the mechanism of Rice and Herzfeld. The most obvious assumption already discussed by ourselves is the recombination of the H atoms at the wall. As is easily seen, this mechanism gives the 2nd to the 3rd order of ethane decomposition while Mareck and McCluer as well as myself most definitely found the first order.

Thus, it seems not to be possible to propose any chain mechanism which agrees reasonably with experiment. Now as formerly it is not denied that a certain percentage of all the decomposing molecules also form radicals, and on account of the new value of Steacie and Phillips just this part is increased, but even now it is only a small fraction of all the reacting molecules. Therefore the chain mechanism seems to be still inadequate to explain the whole process of the decomposition of ethane. We do not want to discuss other decomposition processes in detail. It would lead to the same result though the calculations would probably contain more uncertainties, and, there is no evident reason to assume a behavior substantially different from that of ethane in the decomposition of acetaldehyd, acetone, etc.

[6] Ind. Eng. Chem. **23**, 878 (1931).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Raman Spectrum and Structure of the Metaborate Ion

Ghosh and Das[1] observed two Raman lines scattered by an aqueous solution of sodium metaborate and interpreted them as shifts of 1403 cm^{-1} and 253 cm^{-1} in the 24,705 cm^{-1} and 22,938 cm^{-1} mercury lines, respectively. They ascribed these Raman shifts to the metaborate ion and concluded that it is triatomic, BO_2^-, and nonlinear. This result seems open to serious doubt, since the BO_2^- ion would have sixteen valence electrons and all the triatomic molecules with sixteen valence electrons for which the structure is known are linear.[2]

We have therefore investigated the Raman spectrum of a 5.0 *N*, or nearly saturated, aqueous solution of sodium metaborate. Although we have made very long exposures, using filters to cut out one or the other of the mercury lines 24,705 cm^{-1} and 22,938 cm^{-1} and also complementary filters,[3] we have failed to observe the lines reported by Ghosh and Das. Instead we have found, besides the water bands, three rather sharp Raman lines corresponding to the single shift of 749 ± 1 cm^{-1} in the 24,705, 24,516 and 22,938 cm^{-1} mercury lines. The two strongest of these, and no other Raman lines, were observed also with a 1.4 *N* solution of sodium metaborate.

That the observed Raman shift is produced by the metaborate ion seems beyond doubt. It is true that some metaboric acid is formed by hydrolysis, but its molar concentration in the concentrated solution, as calculated from the known ionization constants of HBO_2 and water, is only 0.1 percent of that of the metaborate ion. Since only a single Raman shift occurs, the metaborate ion must be triatomic, linear and symmetrical, and the shift of 749 cm^{-1} must represent the frequency ν_1 of the totally symmetrical vibration. From the values of ν_1 and the atomic masses it is possible to calculate the force constant k_1 and rough values for the frequency ν_3 of the asymmetrical longitudinal vibration. One finds $k_1 = 5.29 \times 10^5$ dynes/cm, $\nu_3 = 1480$ cm^{-1} for a metaborate ion containing the most abundant boron isotope and $\nu_3 = 1530$ cm^{-1} for BO_2^- with boron of atomic mass 10. These frequencies as well as that of the transverse vibration ν_2 should be observable in infrared absorption.

The problem of determining the electronic structure of the metaborate ion now arises. Two formulas suggest themselves, $\overset{-}{O}-\overset{+}{B}-\overset{-}{O}$ and $O=B=O$, the latter corresponding to the structure assumed for carbon dioxide.[4] We have worked out first-order expressions for the energies, but without actually evaluating a number of integrals it does not seem possible to conclude which form is the more stable. However, the low value of the force constant k_1 favors the structure $\overset{-}{O}-\overset{+}{B}-\overset{-}{O}$ which is also indicated by the chemical behavior of borates.

The formula $\overset{-}{O}-\overset{+}{B}-\overset{-}{O}$ does not seem incompatible with the fact that in crystalline borates the boron atoms are generally surrounded by three oxygen atoms.[5] On the basis of his extensive data on the crystal structure of borates, Zachariasen has suggested that the metaborate ion may have a plane ring structure $(B_3O_6)^{-3}$.[6] This possibility seems ruled out by our results.

An investigation of the Raman spectra of solutions of other borates and of crystalline sodium metaborate is under way. This work has been made possible by grants from the American Association for the advancement of Science and the National Research Council.

J. RUD NIELSEN
N. E. WARD

Department of Physics,
University of Oklahoma,
Norman, Oklahoma,
February 2, 1937.

[1] J. C. Ghosh and S. K. Das, J. Phys. Chem. **36**, 586 (1932).
[2] Cf. W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. **A156**, 654 (1936).
[3] Cf. R. Ananthakrishnan, Nature **138**, 803 (1936).
[4] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 205 (1935).
[5] W. H. Zachariasen, Proc. Nat. Acad. Sci. **17**, 617 (1931); Zeits. f. Krist. **76**, 289 (1931); **88**, 150 (1934); W. H. Zachariasen and J. E. Ziegler, Zeits. f. Krist. **83**, 354 (1932).
[6] This suggestion was made in a letter to one of us. We are indebted to Professor Zachariasen for valuable discussion.

The Internuclear Distance in Te_2

Maxwell and Mosley[1] have recently deduced, from electron diffraction measurements, an internuclear separation in the Te_2 molecule of 2.59 ± 0.02A, in marked disagreement with the value of 2.85A computed from the rotational band spectrum constants.[2] It is perhaps worth noting that the new distance agrees well with the value of 2.61A calculated by the writer's[3] semiempirical equation from the oscillational constants w_e and $w_e x_e$ and a "basic radius" r_1 obtained from the data on I_2. One of the few large discrepancies between experimental r_e values and those calculated in this way is thus removed. Badger's[4] empirical equation leads to $r_e = 2.55$A, also agreeing much better with the electron diffraction value than with the older result.

MAURICE L. HUGGINS

Kodak Research Laboratories,
Rochester, New York,
February 5, 1937.

[1] L. R. Maxwell and V. M. Mosley, Bulletin Am. Phys. Soc. **12**, No. 1, Part 1, 9 (1937) (Abstracts for the North Carolina Meeting).
[2] A. Przeborski, Zeits. f. Physik **63**, 280 (1930); W. Jevons, *Report on Band Spectra of Diatomic Molecules* (Physical Society, London, 1932).
[3] M. L. Huggins, J. Chem. Phys. **3**, 473 (1935); **4**, 308 (1936).
[4] R. M. Badger, J. Chem. Phys. **3**, 710 (1935).

Possible Formation of Hydrogen Bonds in Liquid Mixtures

In a recent communication[1] the writer suggested that some results obtained by him on the infrared absorption of certain binary liquid mixtures might possibly be interpreted as indicating the formation of hydrogen bonds between the two liquids. When liquids containing the hydroxyl group, such as alcohol or water, which probably are already associated through hydrogen bonds, were mixed with some other liquids, such as acetone or methyl cyanide, which contain the strongly electronegative atoms, oxygen or nitrogen, having unshared electron pairs, the fundamental band of the hydroxyl group was found to be shifted to the shorter wave-lengths. There has arisen some question as to whether, in a mixture of liquids in which hydrogen bonds are formed between the liquids, the hydroxyl band would appear at shorter wave-lengths than it would in the pure liquid. Buswell, Deitz, and Rodebush[2] have suggested that one may predict an opposite effect, a shift to the longer wave-lengths of this band. Indeed, such a prediction would be justified were it not likely that the formation of hydrogen bonds in the pure water or alcohol has already shifted the hydroxyl band to the longer wave-lengths and that these bonds are probably broken if and when the H of the hydroxyl group is employed in forming a bond between a molecule of alcohol or water and a molecule of some other liquid. If the molecules of the pure liquid, XOH, are linked in some manner so that both the O and the H of a single hydroxyl group participate in the formation of bonds, as would be the case if large aggregates of molecules are formed, a possibility suggested by Latimer and Rodebush,[3] or if two molecules are joined through a pair of hydrogen bonds, as

$$\begin{array}{l} XO-H \\ \quad\ | \quad | \\ \quad H-OX \end{array}$$

it would seem that one may anticipate a greater shift to the longer wave-lengths of the hydroxyl band than if only the H of the group participated in the bond formation, as it would if the liquid were linked with some other liquid, say a ketone $RC=O$, as $XO-H-O=CR$. This view should explain the resulting shorter wave-length shift of the hydroxyl band in liquid mixtures of this type, and should certainly account for the longer wave-length shift of the $C=O$ band of the second liquid. However, the results would require that in a 1 : 1 mixture of the above-mentioned liquids only a relatively small number of the molecules unite to form the complex, $XO-H-O=CR$. It is possible that in a given mixture complexes of this type together with polymerized and also unassociated molecules of XOH exist in dynamical equilibrium. This may be the explanation of the broadness and also of the variation with concentration of the hydroxyl band.

I cannot see how the above interpretation would conflict with the one given by Buswell, Deitz, and Rodebush to their results. I recognize, however, that there may be other explanations and that more experimental data is needed before the question can be decided.

WALTER GORDY

Mary Hardin-Baylor College,
Belton, Texas,
February 8, 1937.

[1] Walter Gordy, J. Chem. Phys. **4**, 749 (1936).
[2] A. M. Buswell, V. Deitz and W. H. Rodebush, J. Chem. Phys. **5**, 84 (1937).
[3] W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. **42**, 1419 (1920).